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Crystal and Solution Structures of Photochromic Spirobenzothiopyran. First Full Characterization of the Meta-Stable Colored Species

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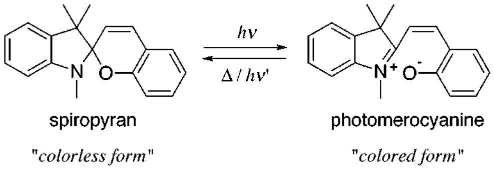
Full elucidation for stable, colorless, and meta-stable colored structures of a new spirobenzothiopyran has been achieved both in the solid state and in a solution. 1′,3′,3′-Trimethyl-6-nitrospiro[(2*H*)-1-benzothiopyran-2,2′-indoline] with an ester group as a substituent at the 8-position of **1-sp** shows photochromism. The blue-green colored species resulted from UV irradiation (365 nm) in one minute and spontaneously bleaches within one minute in acetone and methanol at 27 °C. UV exposure (365 nm) of **1-sp** in methanol for 3 h at room temperature results in the growth of deep blue needlelike single crystals of the open form of spirobenzothiopyran, photomerocyanine **1-pmc**, whose structures in the solid state and in solution were obtained unambiguously. The X-ray structural analysis of **1-pmc** revealed the molecular structure of the zwitterionic photomerocyanine with *s*-trans,*s*-trans conformation. **1-pmc** is soluble to polar solvents and thermally returns to **1-sp**. In the DMSO solution, **1-pmc** is found to return slowly to **1-sp** (**1-pmc** gave only 18% of **1-sp** for 30 min at 22 °C). The detailed NMR studies in DMSO-d_6 including COSY and NOE techniques as well as isotope labeling of the compound showed the structure with *s*-trans,*s*-cis conformation in a solution.

Introduction

Much attention has been paid to photochromic compounds because of potential utility as molecular information devices. Spiropyrans are some of the typical organic photochromic compounds having high extinction coefficients in the near-infrared region and have been widely studied on the basis of chemical, physical, and material points of view.[1] Their photochromic behavior is normally based on the UV irradiation promoted opening of the spiro ring system to produce the colored species and their photo and/or thermal relaxation to regenerate the spiropyrans (eq 1 is depicted as a least motion illustration).



(1)

The elucidation of their real meta-stable structures is one of the current topics in this field. Although time-resolved resonances of UV−vis, Raman, and IR are powerful methods for characterization of the short-lived species,[2] the structural information obtained from these spectroscopic methods is still limited. Studies using negative photochromic spiropyrans[3] and stabilization by hydrogen bonding,[4] by the combination with crown ether or cyclodextrin,[5] and by complexation with chromium[6] are also performed to stabilize and characterize the colored form of spiropyrans. Although association of spiropyran and the photomerocyanine is suggested by UV−vis spectroscopies in nonpolar[7] and polar solvents,[8] attempts to isolate the real meta-stable form of spiropyrans by their UV exposure or placement in an electrical field[9,10] led to

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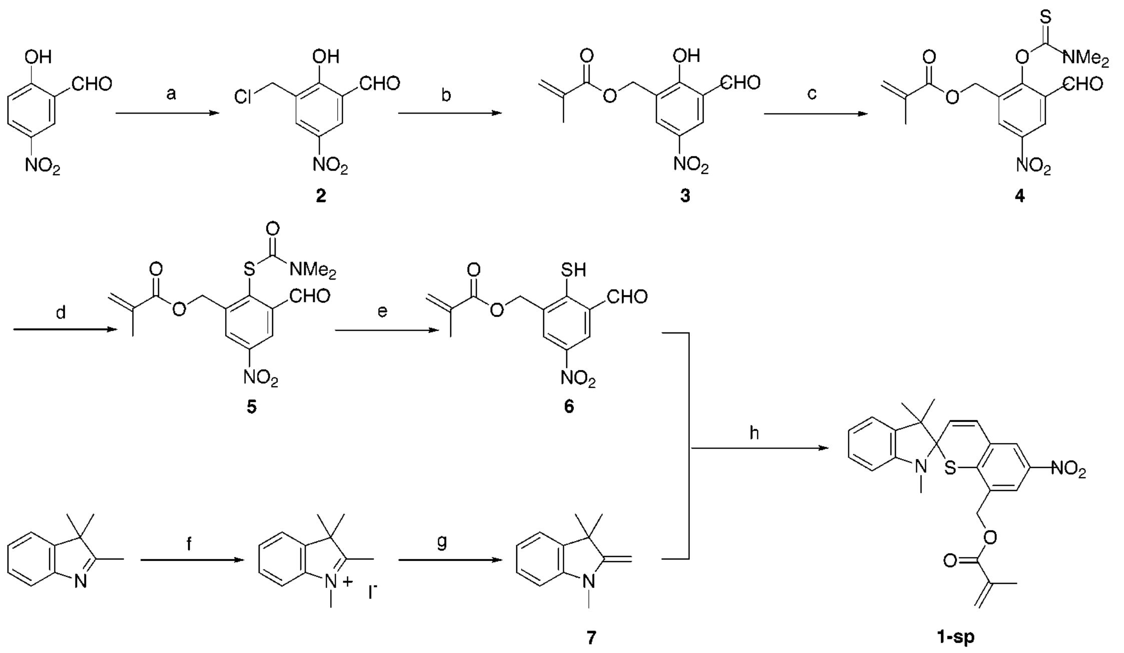
Scheme 1[a]



[a] Reagents and conditions for **1-sp**: (a) $ClCH_2OMe/AlCl_3$, room temperature for 1 h and then reflux for 2.5 h, 72%; (b) 1.5 equiv of silver methacrylate, toluene, reflux for 2 h, 96%; (c) 1.5 equiv of $ClCSNMe_2$, 2 equiv of DABCO, DMF, room temperature for 2 h; 90%; (d) toluene, reflux for 2 h, 55%; (e) MeOH, 0.7 M NaOH, 20 °C, 10 min, 81%; (f) 1 equiv MeI, $CHCl_3$, 80 °C, 21 h, 79%; (g) 1.0 M KOH, room temperature for 1 h, 55%; (h) 1 equiv of **7** to **6**, 2-butanone, 70 °C for 20 h in the dark, 41%.

deposition of the colored form of spiropyrans as an amorphous powder or quasi-crystals. Detailed structural information of these deposits as well as other meta-stable colored forms of spiropyrans has been quite limited. Crystallogaphic studies of photomerocyanine (colored form of spiropyran) of negative photochromic spiropyrans[11] as well as model compounds of nonphotochromic photomerocyanine[12] have provided useful information concerning the meta-stable molecular structure of the normal photochromic spiropyrans. However, full characterization dealing with the meta-stable structure of normal photochromic spiropyrans both in a solid and in solution has not yet been carried out. The present study shows the first full structural analysis of meta-stable photomerocyanine formed by UV irradiation, indicating significant differences between the solid and solution structures.

Results and Discussion

Synthesis and Molecular Structure of Spirobenzothiopyran. The photochromic spirobenzothiopyran, 8-methacryloxymethyl-1′,3′,3′-trimethyl-6-nitrospiro[(2*H*)-1-benzothiopyran-2,2′-indoline] (**1-sp**), was prepared by condensation between 3-methacryloxymethyl-5-nitrothiosalicylaldehyde (**6**) and 1,3,3-trimethyl-2-methyleneindoline (**7**) in 41% yield as outlined in the Scheme 1.[13] Spirobenzothiopyran **1-sp** was fully characterized by NMR, IR, and MS spectra, elemental analysis, and X-ray structural analysis.

Single crystals of **1-sp** suitable for X-ray analysis were obtained as yellow cubes by recrystallization from a mixture of benzene and hexane (1:9).

A single crystal contains two crystallographically independent molecules, which have structures that are basically similar to each other. An ORTEP drawing of one of them is shown in Figure 1. Selected bond distances and angles for **1-sp** are listed in Table 1. The most significant feature in the X-ray structure is the bond distance S(1)−C(8) [1.91(1) Å] being significantly longer than the sum of their covalent radii (1.81 Å).[14] To compensate for this feature, the bond S(1)−C(16) [1.74(1) Å] is shorter than a typical one.

Photochromic Property. Upon exposure of **1-sp** to UV light in polar solvents such as methanol and acetone, the light yellow solution turned to blue-green. The color was spontaneously bleached at room temperature when the irradiation turned off. The thermal bleaching obeys first-order kinetics, whose rate constants at 27.0 °C as well as the absorption maximum (λ_{max}) of the colored form are listed in Table 2.

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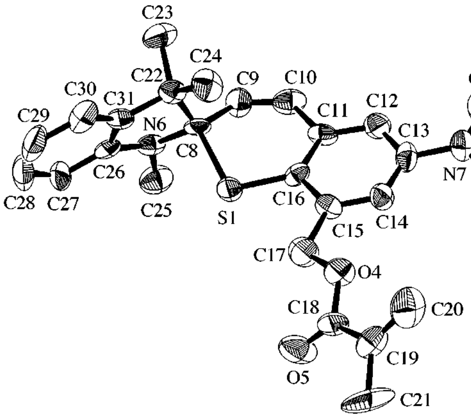

Figure 1. Molecular structure of one of two crystallographically independent molecules of spirobenzothiopyran **1-sp**. Another molecule has basically the same structure. All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Table 1. Selected Bond Distances and Angles for Spirobenzothiopyran 1-sp

	Bond Distances (Å)		
S(1)−C(8)	1.91(1)	S(1)−C(16)	1.74(1)
O(2)−N(7)	1.20(2)	O(3)−N(7)	1.28(2)
N(6)−C(8)	1.42(2)	N(6)−C(25)	1.50(2)
N(6)−C(26)	1.40(2)	N(7)−C(13)	1.43(2)
C(8)−C(9)	1.51(2)	C(8)−C(22)	1.58(2)
C(9)−C(10)	1.27(2)	C(10)−C(11)	1.52(2)
C(11)−C(12)	1.39(2)	C(11)−C(16)	1.40(2)
C(12)−C(13)	1.40(2)	C(13)−C(14)	1.36(2)
C(14)−C(15)	1.35(2)	C(15)−C(16)	1.43(2)
C(22)−C(23)	1.56(2)	C(22)−C(24)	1.53(2)
C(22)−C(31)	1.49(2)	C(26)−C(27)	1.36(2)
C(26)−C(31)	1.42(2)	C(27)−C(28)	1.40(3)
C(28)−C(29)	1.37(3)	C(29)−C(30)	1.39(2)
C(30)−C(31)	1.35(2)		
	Bond Angles (deg)		
C(8)−S(1)−C(16)	105.4(5)	C(17)−O(4)−C(18)	116.0(11)
C(8)−N(6)−C(25)	120.5(10)	C(8)−N(6)−C(26)	110.9(9)
C(25)−N(6)−C(26)	121(1)	O(2)−N(7)−O(3)	120(1)
O(2)−N(7)−C(13)	122(1)	O(3)−N(7)−C(13)	116(1)
S(1)−C(8)−N(6)	105.2(8)	S(1)−C(8)−C(9)	106.9(8)
S(1)−C(8)−C(22)	110.1(8)	N(6)−C(8)−C(9)	112.9(10)
N(6)−C(8)−C(22)	101.9(9)	C(9)−C(8)−C(22)	119.0(10)
C(8)−C(9)−C(10)	128(1)	C(9)−C(10)−C(11)	127(1)

Table 2. Absorption Maxima and Thermal Bleaching Rates for the Photomerocyanine Derived from Spirobenzothiopyran 1-sp in Methanol and Acetone Solution at 27.0 ± 1.0 °C

	λ_{max}/nm	k/s^{-1}
methanol	588	0.06
acetone	673	0.1

The colored species in acetone has an absorption maximum around 670 nm, which extends to about 900 nm. This is one of the longest absorption bands of the organic photochromic compounds and is susceptible to the light generated by a semiconductive laser.[15] The absorption maximum of **1-pmc** in acetone shifted to a wavelength longer by 85 nm than those in more polar methanol. This solvatochromic feature of **1-pmc** can be accounted for by the fact that the ground state of **1-pmc** has a more polarized structure than the exited state, suggesting zwitterionic structure of the colored form.[16]

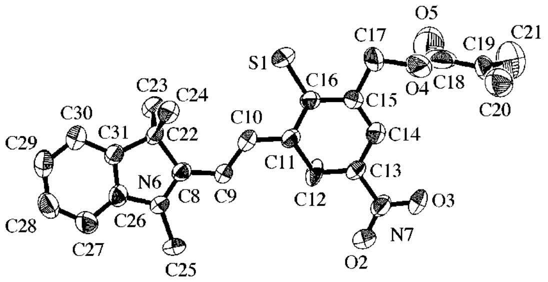

Figure 2. Molecular structure of photomerocyanine **1-pmc**. All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Table 3. Selected Bond Distances and Angles for Spirobenzothiopyran 1-pmc

	Bond Distances (Å)		
S(1)−C(16)	1.701(4)	O(2)−N(7)	1.226(5)
O(3)−N(7)	1.221(4)	N(6)−C(8)	1.316(6)
N(6)−C(25)	1.480(5)	N(6)−C(26)	1.414(4)
N(7)−C(13)	1.450(5)	C(8)−C(9)	1.412(5)
C(8)−C(22)	1.536(5)	C(9)−C(10)	1.352(6)
C(10)−C(11)	1.439(5)	C(11)−C(12)	1.395(5)
C(11)−C(16)	1.446(6)	C(12)−C(13)	1.369(5)
C(13)−C(14)	1.409(6)	C(14)−C(15)	1.362(6)
C(15)−C(16)	1.422(5)	C(22)−C(23)	1.532(7)
C(22)−C(24)	1.545(6)	C(22)−C(31)	1.505(5)
C(26)−C(27)	1.384(7)	C(26)−C(31)	1.375(6)
C(26)−C(31)	1.42(2)	C(27)−C(28)	1.400(3)
C(27)−C(28)	1.400(5)	C(28)−C(29)	1.388(8)
C(29)−C(30)	1.383(7)	C(30)−C(31)	1.389(4)
	Bond Angles (deg)		
C(8)−N(6)−C(25)	125.6(3)	C(8)−N(6)−C(26)	111.9(3)
C(25)−N(6)−C(26)	122.5(4)	O(2)−N(7)−O(3)	122.5(3)
O(2)−N(7)−C(13)	118.5(5)	O(3)−N(7)−C(13)	118.9(4)
N(6)−C(8)−C(9)	121.8(4)	N(6)−C(8)−C(22)	109.2(3)
C(9)−C(8)−C(22)	129.0(4)	C(9)−C(10)−C(11)	127.8(4)
C(10)−C(11)−C(12)	121.9(4)	C(11)−C(12)−C(13)	120.2(4)
N(7)−C(13)−C(12)	117.5(3)	N(7)−C(13)−C(14)	120.9(4)
C(12)−C(13)−C(14)	121.5(3)	C(13)−C(14)−C(15)	119.5(3)
C(14)−C(15)−C(16)	121.5(4)	S(1)−C(16)−C(11)	122.0(3)
S(1)−C(16)−C(15)	120.3(4)	C(11)−C(16)−C(15)	117.7(3)
C(8)−C(22)−C(23)	111.8(4)	C(8)−C(22)−C(24)	112.1(3)
N(6)−C(26)−C(27)	127.6(4)	N(6)−C(26)−C(31)	108.6(4)
C(27)−C(26)−C(31)	123.8(3)	C(26)−C(27)−C(28)	116.1(5)
C(28)−C(29)−C(30)	121.2(4)	C(29)−C(30)−C(31)	118.5(4)

Photoinduced Crystallization of the Meta-Stable Colored Form and the Molecular Structure in the Solid State. We exposed a methanol solution of **1-sp** to UV light for 3 h at 27 °C in a quartz Schlenk tube under nitrogen. Deep blue (almost black) needles (abbreviated as **1-pmc**) grew on the surface of the irradiated area.[17] Tiny crystalline deposits began to form within 30 min, and further exposure grew the crystalline deposits.

Single crystals suitable for X-ray crystallography were selected from the deposits. The molecular structure of **1-pmc** was shown in Figure 2, and the selected bond distances and angles are listed in Table 3.

Two aromatic rings are almost in plane (dihedral angle = 6.5°), indicating the presence of conjugation along two aromatic rings in the *s*-trans,*s*-trans conformation. The coloration for **1-pmc** is ascribed to such a long π-conjugation. The bond distance S(1)−C(16) [1.701(4) Å] shows a typical double-bond character, indicating that the pho-

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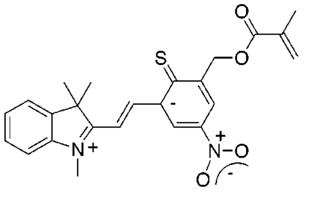
[17] Photographs of crystals of **1-pmc** and the mixed aggregates of **1-pmc** and **1-sp** are available (PDF files) in Supporting Information.

Chart 1



tomerocyanine in the solid state prefers the thione rather than the thiolate structure. The O(2)−N(7) [1.226(5) Å] and O(3)−N(7) [1.221(4) Å] bonds are the same within the experimental error, suggesting contribution of the aci-nitro structure. The bond distances N(6)−C(8) [1.316(6) Å] and C(9)−C(10) [1.352(6) Å] indicate double-bond character, while C(8)−C(9) [1.412(5) Å] and C(10)−C(11) [1.439(5) Å] are relatively longer than these bonds, showing bond alternation. Significant bond alternation is also found in the thiophenyl moiety. The bond distances C(11)−C(16) [1.446(6) Å], C(11)−C(12) [1.395(5) Å], and C(13)−C(14) [1.409(6) Å] are longer than those in C(12)−C(13) [1.369(5) Å] and C(14)−C(15) [1.362(6) Å]. On the other hand, no significant bond alternation is found in the benzo ring of the indolenium moiety. Thus, the crystal structure of **1-pmc** is best regarded as the extensive zwitterionic form as shown in Chart 1.

Of great interest is the blue crystal **1-pmc** being consistent with pure meta-stable photomerocyanine. This shows sharp contrast to the reported quasi-crystals composed of both spiropyrans and photomerocyanines.[10]

The IR spectra and the absorption bands for **1-pmc** involving those for the colorless form **1-sp** for comparison are shown in Figure 3 and Table 4. The IR spectrum of **1-pmc** shows intensive ν_{as}(N−O) and ν_s(N−O) bands at 1579 and 1286 cm^{-1}, respectively. The significant lower shift of the ν_s(N−O) band is due to the aci-nitro contribution in **1-pmc**. This feature is consistent with the X-ray structure. A similar frequency shift of the nitro group is documented for the aggregated photomerocyanine derived from 1′,3′,3′-trimethyl-6-nitrospiro[(2*H*)-1-benzopyran-2,2′-indoline].[9b] An intensive band at 1252 cm^{-1} is assignable to the ν(C=S) band because this signal is characteristic of the photomerocyanine derived from spirobenzothiopyran. A band at 1607 cm^{-1} for **1-sp**, which is due to the *cis*-ν(C=C) band for the benzothiopyran ring, disappears for **1-pmc**, suggesting transformation to the trans form. The other bands are assigned basically according to the literature.[2c,9b,9c,10f,18,19]

The photomerocyanine **1-pmc** is highly thermally stable and is stable for more than one year at room temperature in the solid state, while it immediately bleaches within a minute in solution. Indeed, **1-pmc** is thermally stable below its melting point (113 °C, DSC), and it returns to **1-sp** when heated above the melting point. This significant thermal stability of the meta-stable state is ascribed to the aggregation. Two possible ways for dye aggregation are known. One is the *J* aggregation, where dye dipoles are arranged in a parallel (head-to-head) way, and another is the *H* aggregation, where dyestuff dipoles are arranged in an antiparallel (head-to-tail) way to compensate for its dipole moment.[20] Related cyanines and merocyanines are known to be capable of forming both *J* and *H* aggregates.[21,22] Photomerocyanine generated from spiropyrans is also reported to form both *J* and *H* aggregates in LB films or cast films.[18,19,23] The crystal packing of **1-pmc** shows that the indolinium and the thione rings of two crystallo-

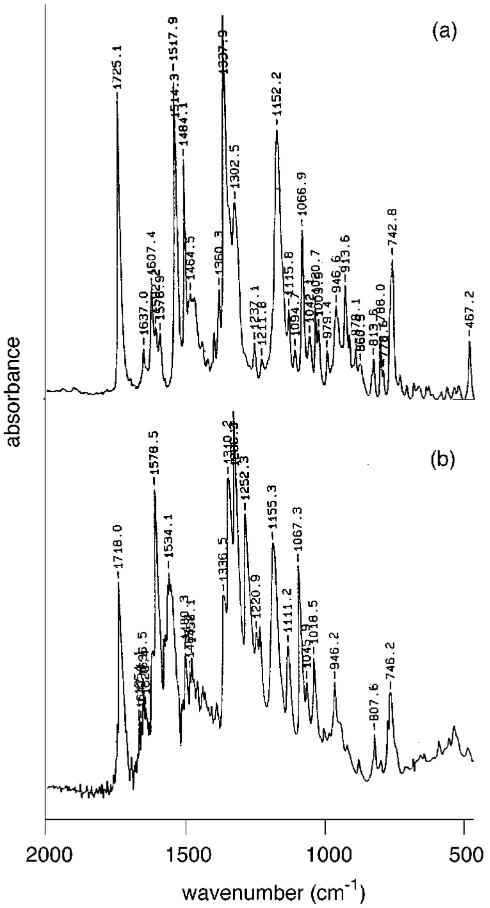


Figure 3. IR absorption spectra for spirobenzothiopyran **1-sp** (a) and photomerocyanine **1-pmc** (b) in the region 450−2000 cm^{-1} in KBr disks.

Table 4. Selected Absorption Bands of IR Spectra for 1-sp and 1-pmc in KBr Disks at Room Temperature (cm^{-1})

1-sp		1-pmc	
1725(s)	νC=O	1718(s)	νC=O
		1654(w)	
1637(w)	νC=C	1637(w)	νC=C
		1629(w)	
1607(m)	νC=C(cis)		
1592(w)	νC=C		
1579(w)	νC=C		
1518(s)	ν_{as}N−O	1579(vs)	ν_{as}N−O
		1534(s)	νC=C
1484(s)	δ_sCH$_2$	1480(m)	δ_sCH$_2$
1458(m)	νC=C		
1338(vs)	ν_sN−O		
		1337(m)	νC=C
1303(m)	νC−N	1310(vs)	νC−N
		1286(vs)	ν_sN−O
		1252(s)	νC=S
1152(s)	ν_sC−C−O	1155(s)	ν_sC−C−O
1067(m)	ν_{as}O−C−C	1067(s)	ν_{as}O−C−C
743(m)	δCH	746(m)	δCH

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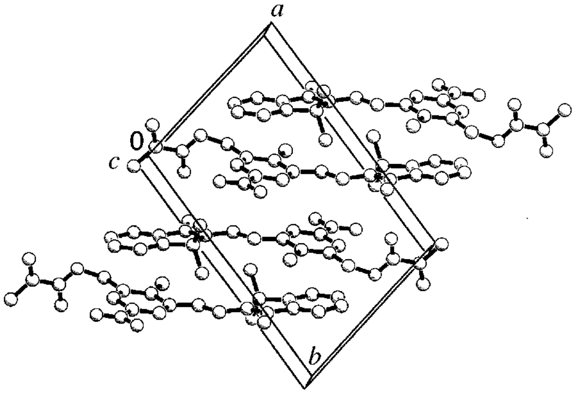

Figure 4. Crystal packing of photomerocyanine **1-pmc** showing alternate dipole stacks.

graphically identical molecules are alternately layered over, although significant intermolecular interaction (less than 3.5 Å) is not found among these atoms (Figure 4). This feature can be accounted for by compensation of the dipole moment in the crystal, and is basically regarded as *H* aggregation involving a 2-fold axis in a unit cell.

Structure of 1-pmc in Solution. Detail analyses of the solution structure of the colored species for normal photochromic spiropyrans have been quite limited because of their general tendency to cause rapid thermal relaxation into the stable colorless form and low molar ratios of the colored species in the photostationary state.[4,24] When the crystals of **1-pmc** were dissolved in polar solvents such as acetone or methanol, rapid and drastic coloration to deep blue-green took place without irradiation. The absorption spectrum of the resulting colored solution was identical to that of the colored species obtained from **1-sp** in acetone or methanol upon irradiation. It should be noted that the crystals of **1-pmc** dissolved in acetone or methanol also thermally bleached spontaneously, and the resulting light yellow solution gave the exactly identical NMR spectrum of the original **1-sp**. The colored species of the spirobenzothiopyran **1-pmc** does not undergo noticeable structural change for 30 min in DMSO at room temperature (only 18% of **1-pmc** returned to **1-sp** for 30 min at 22 °C), which has enabled full spectroscopic determination of the structure in solution. Compound **1-pmc** dissolved immediately thereafter in DMSO-d_6 afforded almost a pure photomerocyanine structure.[25] Figure 5 shows the ^{1}H NMR spectrum of the colored form **1-pmc** in DMSO-d_6 as well as that of the colorless form **1-sp** for comparison. These resonances were unambiguously assigned by using ^{1}H–^{1}H COSY.

The geminal methyl groups at the 3′-position of **1-pmc** appear equivalently as a singlet, while these for **1-sp** are magnetically inequivalent. This feature indicates that the spiro linkage is cleaved to give a planer structure in the former structure. A new singlet at 4.10 ppm is assigned as the N-*Me* group, which notably shifted to a lower field than **1-sp** (2.93 ppm in DMSO-d_6). This significant low-field shift arises from the cationic charge on the nitrogen in the zwitterionic structure. Indeed, the resonance is comparable to the N$^+$-*Me* group in the cationic analogue 1,2,3,3-tetramethylindolenium iodide (4.20 ppm). This zwitterionic feature is consistent with the significant solvent effect of the colored species on the absorption maximum, where the λ_{max} of **1-pmc** in acetone shifted to a wavelength longer by 85 nm than that in methanol. Two characteristic doublets at 7.63 (d, $J = 16.0$ Hz, 1H) and 9.51 ppm (d, $J = 16.0$ Hz, 1H) are assignable to the alkenylic protons, and the large coupling constant indicates that they are mutually trans. Therefore, only four candidates are possible for structures in a solution as illustrated in Chart 2.

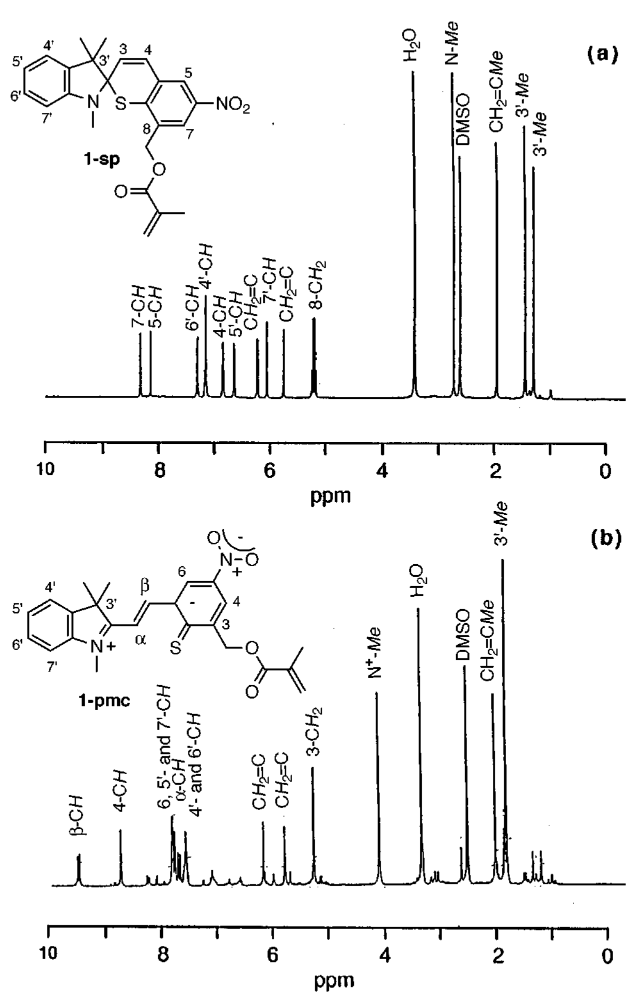

Figure 5. ^{1}H NMR spectra for spirobenzothiopyran **1-sp** (a) and photomerocyanine **1-pmc** (b) in DMSO-d_6 at room temperature.

To assign the α- and β-proton signals in the ^{1}H NMR spectrum, we prepared the isotope-labeled **1-*d*$_1$-pmc** in 12% yield on the basis of **1-*d*$_1$-sp** (as outlined in Scheme 2), whose α-alkenylic proton is exclusively deuterated with 50 atom % D content.

The ^{1}H NMR spectrum of **1-*d*$_1$-pmc** clearly indicates a slightly broad singlet (likely due to the $^3J_{HD}$ coupling) at 9.51 ppm, while the intensity of the signal at 7.63 ppm for **1-pmc** was significantly decreased by the deuteration. Thus, the former is unambiguously assigned to the β-alkenylic proton and the latter is assigned to the α-alkenylic one.

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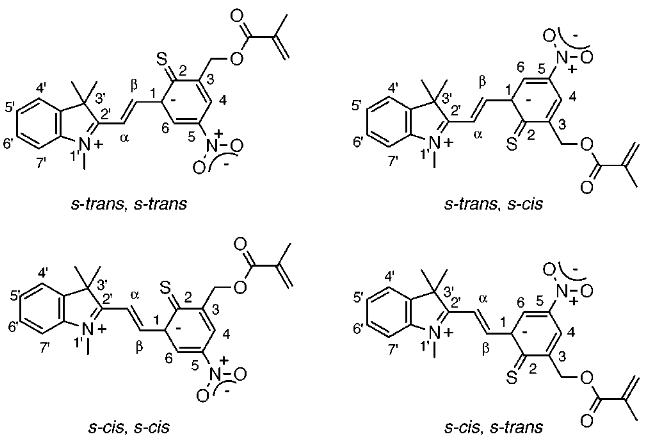
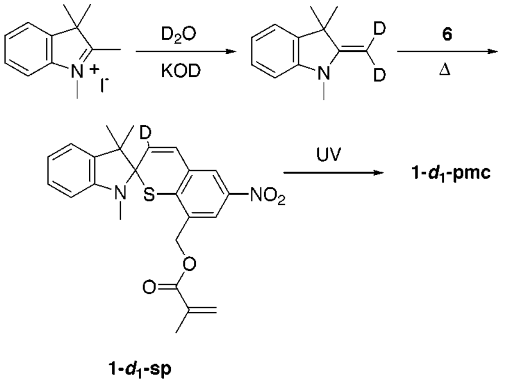
(25) Residual peaks are identical to the colorless form **1-sp**.

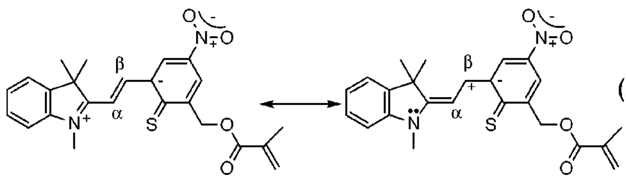
Chart 2



Scheme 2



NOE experiments for **1-pmc** were carried out to determine the molecular conformation in solution. Irradiation of the geminal methyl groups at the 3′-position led to an exclusive enhancement on the integration of the β-alkenylic proton by 31% and slight reduction on the integration of the proton at the 6-position by −9.0%. This fact indicates that the geminal methyl and β-alkenylic protons are close to each other and rules out the *s*-cis,*s*-cis and *s*-cis,*s*-trans forms in Chart 2, whose β-proton is farther than their α-proton from the geminal methyls. The negative NOE for the 6-proton suggests a linear alignment among the geminal methyls, the β-alkenyl proton, and the proton at the 6-position. While no observable NOE was detected by irradiations to the N-*Me* protons and the 4-proton, irradiation to the 6-proton led to enhancement on the integration of the β-proton by 9.5%. From these experiments, we can conclude that the solution structure for **1-pmc** has the *s*-trans,*s*-cis conformation. It is interesting that **1-pmc** has the *s*-trans,*s*-cis photomerocyanine structure in a solution, while it has the *s*-trans,*s*-trans photomerocyanine structure in the crystal. Abe and Irie reported MNDO-PM3 calculations for the photomerocyanine derived from 1′,3′,3′-trimethyl-6-nitrospiro[(2*H*)-1-benzopyran-2,2′-indoline], where they pointed out that the *s*-trans,*s*-trans conformer is the most stable product, but only the *s*-trans,*s*-cis conformer has been reported by NMR.[26,27] Our NMR experiments also show the *s*-trans,*s*-cis conformer in a solution. One of possible reasons for this arises from the intermolecular interaction in solution because such calculations do not take into account such an interaction. Indeed, the β-alkenylic proton appears in a significantly low field at 9.51 ppm, while the α-alkenylic proton shows little deshielding effect (7.63 ppm). This feature suggests that the β-protons have intermolecular hydrogen bonding with a solvent molecule or another **1-pmc** in solution. Contrary to the β-proton, the α-proton is expected to be less protic because of its position in the conjugation system as depicted in eq 2. This hydrogen bonding is likely due to stabilization of the *s*-trans,*s*-cis conformer in solution.



(2)

Formation of Mixed Aggregates of 1-sp and 1-pmc. When a hexane solution of **1-sp** was irradiated by UV light for 3 h at 27 °C, a light orange crystalline precipitate grew on the surface of vessel of the irradiated beam spot in 55% yield.[17] This orange precipitate also afforded a deep green-colored solution without irradiation when it was dissolved into polar solvents such as acetone or methanol. The NMR spectrum of the orange deposit shows a mixture of **1-sp** and **1-pmc**. On the basis of the integration ratio of the ^{1}H NMR spectrum in DMSO-d_6, the orange precipitate contains **1-pmc** up to 43%. Therefore, this deposit is most likely due to a composite between **1-sp** and **1-pmc** in a 1:1 ratio. Similar composites are reported by Krongauz and co-workers[10a,b] as quasi-crystals between spiropyran and photomerocyanine in 1:1 and 2:1 ratios. Contrary to the NMR data, the IR spectrum of this orange precipitate is basically identical to that of **1-sp**. Therefore, the conformation and/or polarization of **1-pmc** in this mixture may be different from that in the pure crystals of **1-pmc**.[28] This significant solvent effect in the formation of the deposits is also likely due to the concentration of the photogenerated colored form **1-pmc** upon irradiation. Because **1-pmc** cannot be stabilized by solvation in hexane and the concentration of photogenerated **1-pmc** is therefore quite low, the short-lived zwitterionic **1-pmc** would interact with another colorless species **1-sp**, rather than another **1-pmc**, by Coulombic interaction to form such a mixed aggregate.

Conclusion

The present study reveals the formation of single crystals of the pure meta-stable photomerocyanine **1-pmc** in *s*-trans,*s*-trans conformation by photoinduced crystallization from a spirobenzothiopyran solution. Such photoinduced crystallization of photomerocyanine shows sharp contrast to the previously reported deposits composed of a mixture of spiropyran and photomerocyanine. In the pure crystals of the colored form, **1-pmc** has the zwitterionic structure bearing thione and aci-nitro contribution. The crystal packing clearly shows that the

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(26) Abe, Y.; Nakao, R.; Horii, T.; Okada, S.; Irie, M. *J. Photochem. Photobiol. A: Chem.* **1996**, *95*, 209−214.

(27) After publication of ref 26, the *s*-trans,*s*-trans photomerocyanine derivative was observed by ^{1}H NMR spectrum (see ref 24).

(28) Recently, some spiropyrans have been found to show the ring opening with a heterolytic C−O bond cleavage mechanism in a polar solvent and with an electrocyclic ring-opening mechanism in nonpolar solvents: Swansburg, S.; Buncel, E.; Lemieux, R. P. *J. Am. Chem. Soc.* **2000**, *122*, 6594−6600.

dipole moment of **1-pmc** is compensated for by the intermolecular interaction. Contrary to this fact, **1-pmc** is found to have a rigid *s*-trans,*s*-cis conformation in solution. The NMR spectrum showed significant deshielding of the β-alkenylic proton, suggesting intermolecular hydrogen bonding. Such a significant difference concerning structures of meta-stable photomerocyanine in the solid and in solution is now revealed. This work will provide extensive information on the studies of photochromic spiropyrans.

Experimental Section

General. Synthesis and characterization of spirobenzothiopyrans and their precursors were carried out under air unless otherwise noted. UV exposure to form **1-pmc** was performed under a nitrogen atmosphere. ^{1}H and ^{13}C{^{1}H} NMR spectra and COSY were recorded on Bruker AM-400 (400.13 MHz for ^{1}H), JEOL FX-90Q (89.55 MHz for ^{1}H), or JEOL PMX-60Si (60 MHz for ^{1}H) instruments. IR spectra were recorded on a Perkin-Elmer FT-1600 Fourier transfer spectrometer. UV−vis absorption spectra were measured by a Shimadzu UV-265FW instrument. UV irradiation was performed by a Ushio 500D (500 W) high-pressure mercury lamp in conjunction with HOYA HA-30 and U-350 band-pass filters to give a light emission at 365 nm. Mass spectra were obtained by a Shimadzu QP-1000 spectrometer with the electron impact method. DSC analyses were carried out by a Seiko Instruments DSC-20 apparatus.

Et_2O, hexane, benzene, and toluene were distilled from Na/benzophenone ketyl as an indicator under nitrogen. Methanol was distilled over $Mg(OMe)_2$ under nitrogen. *N*,*N*-Dimethylformamide (DMF) was distilled from molecular sieves (4A) under reduced pressure. $CDCl_3$ was dried over molecular sieves (4A). DMSO-d_6 was dried over CaH_2 at 120 °C for 4 h and then distilled under reduced pressure. Anhydrous $AlCl_3$ was sublimed under reduced pressure with a coldfinger trap. 5-Nitrosalicylaldehyde and 2,3,3-trimethylindolenine were purchased from TCI, and *N*,*N*-dimethylthiocarbamoyl chloride was purchased from Aldrich; each was used as received.

3-Chloromethyl-5-nitrosalicylaldehyde (2). 5-Nitrosalicylaldehyde (2.00 g, 12.0 mmol) was dissolved in dry chloromethyl methyl ether (20 mL), and then freshly sublimed aluminum trichloride (8.01 g, 60.0 mmol) was added under nitrogen. The reaction mixture was stirred for an hour at room temperature and then was refluxed for 2.5 h. After the reaction, ice cooled water was added into the reaction mixture and the resulting off-white residue was collected. Recrystallization of the off-white solid from hot hexane (500 mL) gave colorless needles of **2** in 72% yield (1.86 g, 8.63 mmol). ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.7 (s, C*H*$_2$Cl, 2H), 8.5 (s, aromatic, 2H), 10.0 (s, C*H*O, 1H), 12.1 (s, O*H*, 1H).

Silver Methacrylate. Methacrylic acid (5.12 g, 60.6 mmol) was added into ice-cooled ammonium water (27%, 12 mL). After stirring for 30 min at room temperature, the reaction mixture was evaporated until the ammonia odor disappeared. Silver nitrate (11.25 g, 66.2 mmol) in water was added into the solution and stirred overnight. The white precipitate was filtered, washed with water repeatedly, and dried under vacuum to give a white powder of silver methacrylate in 71% (8.37 g, 43.3 mmol). IR (KBr, cm^{-1}): 3000 (w, νC−H), 2950 (w, νC−H), 1650 (w, νC=C), 1550 (s, ν_{as}C−O), 1375 (s, ν_sC−O).

3-Methacryloxymethyl-5-nitrosalicylaldehyde. Compound **2** (0.20 g, 0.93 mmol) was reacted with silver methacrylate (0.29 g, 1.5 mmol) in dry toluene at 120 °C for 2 h under nitrogen. Hot filtration through a Celite pad followed by evaporation of the resulting solution gave a yellow solid of **3** in 96% yield (0.25 g, 0.89 mmol). ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.0 (m, CH$_2$=C*Me*, 3H), 5.3 (s, −C*H*$_2$−, 2H), 5.7 (m, C*H*$_2$=CMe, 1H), 6.2 (m, C*H*$_2$=CMe, 1H), 8.5 (s, aromatic, 2H), 10.0 (s, −C*H*O, 1H), 12.0 (br, O*H*, 1H). IR (KBr, cm^{-1}): 3050 (w, ν aromatic C−H), 2950 (w, νC−H), 2850 (w, νC−H), 1705 (s, νC=O), 1660 (s, νC=O), 1600 (s, aromatic), 1520 (s, ν_{as}N−O), 1345 (s, ν_sN−O), 820 (s, aromatic). Mp: 127.0−129.0 °C.

3-Methacryloxylmethyl-2-*O*-(*N*,*N*-dimethylthiocarbamoyl)-5-nitrosalicylaldehyde (4). Compound **3** (137.6 mg, 0.519 mmol) reacted with *N*,*N*-dimethylthiocarbamoyl chloride (96.2 mg, 0.779 mmol) in the presence of 1,4-diazabicyclo[2.2.2]-octane (111.7 mg, 1.05 mmol) in dry DMF (3 mL) at room temperature for 2 h. The yellow solution turned into a dark brown suspension during the reaction. The resulting solution was filtered through a Celite pad, and the light brown solution was evaporated to dryness. The obtained brown tar was dissolved into ethyl acetate, washed with saturated aqueous sodium chloride, and dried over anhydrous magnesium sulfate. Evaporation of the solution to dryness gave a reddish brown tar of **4** in 90% yield (200 mg, 0.57 mmol). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.0 (m, *CH*$_2$=C*Me*, 3H), 3.5 (s, N*Me*, 6H), 5.3 (s, −C*H*$_2$−, 2H), 5.7 (m, CH$_2$=CMe, 1H), 6.2 (m, C*H*$_2$=CMe, 1H), 8.6 (d, aromatic, J = 3 Hz, 1H), 8.7 (d, aromatic, J = 3 Hz, 1H), 10.0 (s, C*H*O, 1H).

3-Methacryloxymethyl-2-*S*-(*N*,*N*-dimethylthiocarbamoyl)-5-nitrosalicylaldehyde (5). Compound **4** (9.86 g, 28.8 mmol) dissolved in dry toluene was refluxed for 2 h. Evaporation of the solution gave a brown tar. Silicagel column chromatography eluted with ethyl acetate/benzene (1/9) gave pure **5** as light yellow crystals in 55% yield (5.61 g, 15.9 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00 (s, CH$_2$=C*Me*, 3H), 3.03 (s, N*Me*, 3H), 3.22 (s, N*Me*, 3H), 5.47 (s, −C*H*$_2$−, 2H), 5.68 (s, C*H*$_2$=CMe, 1H), 6.22 (s, C*H*$_2$=CMe, 1H), 8.55 (d, aromatic, J = 2.7 Hz, 1H), 8.77 (d, aromatic, J = 2.7 Hz, 1H), 10.39 (s, C*H*O, 1H). Mp: 93−98 °C.

3-Methacryloxymethyl-5-nitrothiosalicylaldehyde (6). Compound **5** (486.5 mg, 1.38 mmol) was dissolved into methanol (50 mL), and 0.7 M NaOH (aqueous) was added dropwise into the solution. The solution was stirred at 20 °C for 10 min during which the light yellow solution turned red. The hydrolysis took place within 10 min, and prolonged reaction afforded corresponding acetals. HCl (aqueous, 1 M) was added into the reaction mixture, and then the product was extracted with Et_2O. The extract was washed with saturated NaCl (aqueous) and dried over anhydrous sodium sulfate. Evaporation of the solution to dryness gave a light yellow powder in 81% (34.1 mg, 1.12 mmol). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.0 (s, CH$_2$=C*Me*, 3H), 5.3 (s, −C*H*$_2$−, 2H), 5.7 (s, C*H*$_2$=CMe, 1H), 6.2 (s, C*H*$_2$=CMe, 1H), 8.2 (br. S*H*, 1H), 8.4 (d, aromatic, J = 2 Hz, 1H), 8.5 (d, aromatic, J = 2 Hz, 1H), 10.0 (s, C*H*O, 1H).

1,2,3,3-Tetramethylindolenium Iodide. 2,3,3-Trimethylindoleniune (1.889 g, 11.86 mmol), chloroform (15 mL), and methyl iodide (1.804 g, 12.71 mmol) were added into an ampule tube. The ampule tube was sealed by a torch and heated at 80 °C for 21 h. The resulting pink powder was filtered and washed with ice-cooled chloroform and then Et_2O repeatedly to give a white powder of 1,2,3,3-tetramethylindolenium iodide in 75% yield (2.69 g, 8.18 mmol). ^{1}H NMR (60 MHz, D_2O): δ 1.7 (s, 3-*Me*, 6H), 2.9 (s, 2-Me, 3H), 4.0 (s, N*Me*, 3H), 7.6 (br, aromatic 4H).

1,3,3-Trimethyl-2-methyleneindoline (7). 1,2,3,3-Tetramethylindolenium iodide (901.6 mg, 2.992 mmol) was added into a solution of potassium hydroxide (1.0 M, 10 mL). The suspension stirred for an hour at room temperature during which the suspension turned into a yellow oil. The resulting oil was extracted with Et_2O and washed with saturated NaCl (aqueous) repeatedly followed by drying over anhydrous sodium sulfate. Evaporation of the solvent gave a light orange liquid of 1,3,3-trimethyl-2-methyleneindoline in 55% (286.8 mg, 1.655 mmol). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.2 (s, 3-*Me*, 6H), 2.9 (s, N*Me*, 3H), 3.8 (s, 2-C*H*$_2$, 2H), 6.3−7.1 (m, aromatic, 4H). The isotope-labeled analogue 1,3,3-trimethyl-2-dideuteriomethyleneindoline was similarly prepared by using D_2O and KOD in 90% yield. On the basis of integration of the ^{1}H NMR spectrum, the content of deuterium is found to be 32% for indoline-d_0, 18% for indoline-d_1, and 50% for indoline-d_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 3-*Me*, 3H), 3.03 (s, N-*Me*, 3H), 6.53 (d, 7-C*H*, *J* = 7.8 Hz, 1H), 6.75 (t, 5-C*H*, *J* = 7.4 Hz, 1H), 7.08 (d, 4-C*H*, *J* = 7.2 Hz, 1H), 7.13 (t, 6-CH, *J* = 7.8 Hz, 1H).

8-Methacryloxylmethyl-1′,3′,3′-trimethyl-6-nitrospiro-[(2*H*)-1-benzothiopyran-2,2′-indoline] (1-sp). 1,3,3-Trimethyl-2-methyleneindoline (355.7 mg, 2.06 mmol) in 2-butanone (3 mL) was added into a 2-butanone solution (10 mL) of 3-methacryloxymethyl-5-nitrothiosalicylaldehyde (610.0 mg, 2.17 mmol). The reaction mixture was heated at 70 °C for 20 h in the dark. After evaporation of solvent, the resulting red wax was purified by silicagel column chromatography in the dark, eluting with a mixture of benzene/hexane (1/1). Recrystallization of the resulting yellow solid from a mixture of benzene/hexane (1/1) gave yellow cubes in 41% yield (374 mg, 0.858 mmol). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.24 (s, 3′-*Me*, 3H), 1.39 (s, 3′-*Me*, 3H), 1.96 (s, CH$_2$═C*Me*, 3H), 2.68 (s, N*Me*, 3H), 5.17 (d, 8-C*H*$_2$-, *J* = 14 Hz, 1H), 5.24 (d, 8-C*H*$_2$-, *J* = 14 Hz, 1H), 5.61 (s, C*H*$_2$═CMe, 1H), 6.05 (d, 3-C*H*, *J* = 11.0 Hz, 1H), 6.17 (s, C*H*$_2$═CMe, 1H), 6.51 (d, 7′-C*H*, *J* = 7.6 Hz, 1H), 6.67 (t, 5′-C*H*, *J* = 7.6 Hz, 1H), 6.97 (d, 4-C*H*, *J* = 11.0 Hz, 1H), 7.07 (d, 4′-C*H*, *J* = 7.6 Hz, 1H), 7.17 (t, 6′-C*H*, *J* = 7.6 Hz, 1H), 8.02 (d, 5-C*H*, *J* = 2.3 Hz, 1H), 8.09 (d, 7-C*H*, *J* = 2.3 Hz, 1H). IR (CCl$_4$, cm^{-1}): 3033 (w, ν aromatic C−H), 2964 (w, νC−H), 2868 (w, νC−H), 1725 (s, νC═O), 1637 (w, νC═C), 1607 (m, νC═C), 1518 (s, ν_{as}N−O), 1484 (s, δ_sCH$_2$), 1338 (vs, ν_sN−O), 1152 (s, ν_sC−C−O), 1067 (m, ν_{as}O−C−C), 743 (m, δCH). MS (EI, 70 eV) *m*/*z*: 436 (M$^+$). Mp (DSC): 111−116 °C. Anal. Calcd.: C, 66.04; H, 5.54; N, 6.42%. Found: C, 65.91; H, 5.42; N, 6.29%. The isotope-labeled compound **1-*d*$_1$-sp** was also prepared analogously in 22% yield (50 atom % D). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.24 (s, 3′-*Me*, 3H), 1.39 (s, 3′-*Me*, 3H), 1.96 (s, CH$_2$═C*Me*, 3H), 2.68 (s, N*Me*, 3H), 5.17 (d, 8-C*H*$_2$-, *J* = 14 Hz, 1H), 5.24 (d, 8-C*H*$_2$-, *J* = 14 Hz, 1H), 5.61 (s, C*H*$_2$═CMe, 1H), 6.17 (s, C*H*$_2$═CMe, 1H), 6.51 (d, 7′-C*H*, *J* = 7.6 Hz, 1H), 6.67 (t, 5′-C*H*, *J* = 7.6 Hz, 1H), 6.96 (br.s, 4-C*H*, 1H), 7.07 (d, 4′-C*H*, *J* = 7.6 Hz, 1H), 7.17 (t, 6′-C*H*, *J* = 7.6 Hz, 1H), 8.02 (d, 5-C*H*, *J* = 2.3 Hz, 1H), 8.09 (d, 7-C*H*, *J* = 2.3 Hz, 1H). MS (EI, 70 eV) *m*/*z*: 437 (M$^+$).

Photoinduced Crystallization of Photomerocyanine 1-pmc from Methanol. A methanol solution (32 mL) of **1-sp** (108.8 mg, 0.25 mmol) was exposed to UV light (365 nm) at 27 °C for 3 h under nitrogen in a Schlenk tube. From the surface of the irradiated beam spot, deep blue (almost black) needles were obtained and washed with methanol followed by drying under vacuum. Yield: 5.4% (5.9 mg, 0.014 mmol). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 1.79 (s, 3′-*Me*, 6H), 1.99 (s, CH$_2$═C*Me*, 3H), 4.10 (s, N*Me*, 3H), 5.27 (s, 3-C*H*$_2$-, 2H), 5.79 (s, C*H*$_2$═CMe, 1H), 6.16 (s, C*H*$_2$═CMe, 1H), 7.58 (m, 4′-C*H* and 6′-C*H*, 2H), 7.63 (d, α-C*H*, *J* = 16.0 Hz, 1H), 7.62 (m, 5′-C*H* and 7′-C*H*, 2H), 7.78 (s, 6-C*H*, 1H), 8.74 (s, 4-C*H*, 1H), 9.51 (d, β-C*H*, *J* = 16.0 Hz, 1H). IR (KBr, cm^{-1}): 3014 (w, ν aromatic C−H), 2976 (w, νC−H), 2932 (w, νC−H), 1718 (s, νC═O), 1637 (w, νC═C) 1579 (vs, ν_{as}N−O), 1534 (s, νC═C), 1480 (m, δ_sCH), 1458 (m, νC═C), 1310 (vs, νC−N), 1286 (vs, ν_sN−O), 1252 (s, νC═S), 1155 (s, ν_sC−C−O), 1067 (s, ν_{as}O−C−C), 746 (m, δCH). MS (EI, 20 eV) *m*/*z*: 436 (M$^+$). Mp (DSC) = 113 °C (converted to **1-sp**). The isotope-labeled compound **1-*d*$_1$-pmc** was also prepared analogously in 12% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 1.79 (s, 3′-*Me*, 6H), 1.99 (s, CH$_2$═C*Me*, 3H), 4.10 (s, N*Me*, 3H), 5.27 (s, 3-C*H*$_2$-, 2H), 5.79 (s, C*H*$_2$═CMe, 1H), 6.16 (s, C*H*$_2$═CMe, 1H), 7.58 (m, 4′-C*H* and 6′-C*H*, 2H), 7.62 (m, 5′-C*H* and 7′-C*H*, 2H), 7.78 (s, 6-C*H*, 1H), 8.74 (s, 4-C*H*, 1H), 9.51 (br.s, β-C*H*, 1H). MS (EI, 20 eV) *m*/*z*: 437 (M$^+$).

Formation of Mixed Aggregates of 1-sp and 1-pmc from Hexane. A hexane solution (34 mL) of **1-sp** (201.2 mg, 0.461 mmol) was exposed to UV light (365 nm) at 27 °C under nitrogen for 3 h in a quartz Schlenk tube. From the surface of the irradiated beam spot, a light orange crystalline powder was formed in 55% yield (110.0 mg, 0.250 mmol). IR (KBr, cm^{-1}): 2962 (w, νC−H), 1725 (vs, νC═O), 1637 (w, νC═C), 1606 (w, C═C), 1518 (s, ν_{as}N−O), 1337 (s, ν_sN−O), 1155 (s, ν_{as}C−O), 1067 (s, ν_sC−O), 746 (s, δC−H). MS (EI, 20 eV) *m*/*z*: 436 (M$^+$).

Crystallographic Studies. The crystallographic data were measured on a Rigaku four-circle diffractometer AFC-5S using Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator. The unit cell dimensions were obtained by a least-squares fit of 25 centered reflections. Intensity data were collected using the ω-2θ technique to a maximum 2θ of 45.0 °. The scan rates were 4.0 deg/min for **1-sp**, and 4.0 deg/min (2θ < 35.0°) and 2.0 deg/min for **1-pmc.** Three standard reflections were monitored in every 200 reflections. No systematic variations in intensity were found. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the CRYSTAN direct methods. Crystallographic Parameters are listed as follows. **1-sp**: formula = $C_{24}H_{24}N_2O_4S$, formula weight = 436.52, crystal system = monoclinic, space group = *Pc*, a = 12.893(2) Å, b = 14.117(4) Å, c = 12.222(2) Å, β = 91.91(1)°, V = 2223.3(8) Å^3, Z = 4, μ = 1.713 cm^{-1}, D_{calcd} = 1.305 g cm^{-3}, D_{found} = 1.31 g cm^{-3} (C_6H_{14}:CCl_4), crystal size = 0.1 × 0.1 × 0.2 mm, unique reflections = 2669, used reflections [$F_o > 3\sigma(F_o)$] = 2070, $R(R_w)$ = 0.068 (0.069). **1-pmc**: formula = $C_{24}H_{24}N_2O_4S$, formula weight = 436.52, crystal system = triclinic, space group = $P\bar{1}$, a = 9.762(7) Å, b = 13.495(8) Å, c = 9.689(5) Å, α = 91.31(5)°, β = 91.91(1)°, γ = 99.21(6)°, V = 1106(1) Å^3, Z = 2, μ = 1.704 cm^{-1}, D_{calcd} = 1.31 g cm^{-3}, crystal size = 0.75 × 0.21 × 0.10 mm, unique reflections = 2370, used reflections [$F_o > 3\sigma(F_o)$] = 1846, $R(R_w)$ = 0.071 (0.073).

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Supporting Information Available: X-ray crystallographic data for **1-sp** and **1-pmc** and photographs of the photomerocyanine cystals **1-pmc** from a methanol solution and the mixed aggregates of **1-pmc** and **1-sp** from a hexane solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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