7-Trifluoromethylquinoline-Functionalized Luminescent Photochromic Spiropyran with the Stable Merocyanine Species Both in Solution and in the Solid State

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A new spiropyran (**SP2**) with the stable merocyanine form (**MC2**) both in solution and in the solid state at room temperature was designed and synthesized. The stability of **MC2** is believed to be due to the electron-withdrawing effect of both the quinoline and the trifluoromethyl groups. ^{1}H NMR spectra indicate that the ratio of the open form vs the closed form of **SP2** is dependent on the polarity of solvents. Single crystals composed of only the open form (**MC2**) were successfully obtained. X-ray structural analysis indicates that except trifluoromethyl and two methyl groups **MC2** is completely planar with an *s-trans,s-cis* conformation. It should be noted that this is the first report of the X-ray crystal structure of the pure open form of spiropyran. **MC2** can be slowly transformed into **SP2** at −30 °C or lower temperature, and the process is accelerated by visible light irradiation. This special photochromic behavior can be explained by the calculated thermodynamic data. The spectral properties of **SP2/MC2** in the presence of different metal ions are also studied, and the results show the potential application of **SP2/MC2** in sensing metal ions.

Introduction

As one of the most promising families of photochromic compounds, spiropyran molecules have been extensively investigated, mainly due to their potential application in the area of molecular sensors, switches, and information processors.[1] Uniquely, spiropyran can undergo reversible structural transformation among the three states as shown in Scheme 1, accompanying the significant changes of the characteristic photochemical and photophysical properties, in response to external inputs such as light, proton, and metal ions.[2−7] By taking advantage of these properties of spiropyran, molecular systems with spiropyran have been configured to mimic the functions of several integrated logic gates, and moreover, communication networks have been proposed in recent years.[6,7] However, the application of spiropyran in these areas is hindered by the fact that its open merocyanine form (**MC** in Scheme 1) is thermally unstable. Thus, stabilization and clear elucidation of their real metastable structure are crucial topics in this context.

Although the open form of spiropyran is not thermally stable, attempts have been made to elucidate its structure by using the powerful methods for characterization of the short-lived species such as time-resolved spectroscopy of UV−vis, Raman, and IR.[8] Studies using negative photochromic spiropyrans and nonphotochromic photomerocyanines as model compounds have been also

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(1) (a) *Molecular Electronic Devices*; Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds.; Elsevier: Amsterdam, 1988. (b) *Nanotechnology*; Crandall, B. C., Lewis, J., Eds.; MIT Press: Cambridge, MA, 1992. (c) Drexler, E. *Nanosystems: Molecular Machinery*, *Manufacturing and Computation*; Wiley: New York, 1992. (d) Credi, A.; Balzani, V.; Langford, S.; Stoddart, J. *J. Am. Chem. Soc.* **1997**, *119*, 2679−2681. (e) Czarnik, A. W. *Curr. Biol.* **1995**, *2*, 423. (f) Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302. (g) Valeur, B.; Bardez, E. *Chem. Br.* **1995**, 216. (h) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.

(2) (a) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: New York, 2001. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (c) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741. (d) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777.

(3) (a) Inoue, M.; Akamatsu, K.; Nakazumi, H. *J. Am. Chem. Soc.* **1997**, *119*, 9160. (b) Dvornikov, A. S.; Malkin, J.; Rentzepis, P. M. *J. Phys. Chem.* **1994**, *98*, 6746.

(4) (a) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421. (b) Willner, I. *Acc. Chem. Res.* **1997**, *30*, 347.

(5) (a) Wojtyk, J. T. C.; Kazmaier, P. M.; Buncel, E. *Chem. Commun.* **1998**, 1703. (b) Wojtyk, J. T. C., Kazmaier, P. M.; Buncel, E. *Chem. Mater.* **2001**, *13*, 2547. (c) Wojtyk, J. T. C.; Wasey, A.; Kazmaier, P. M.; Hoz, S.; Buncel, E. *J. Phys. Chem. A* **2000**, *104*, 9046.

(6) (a) Raymo, F. M.; Giorgani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651. (b) Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401 and further reference therein. (c) Raymo, F. M.; Giordani, S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4941. (d) Raymo, F. M.; Alvarado, R. J.; Giordani, S.; Cejas, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 2361.

(7) (a) Guo, X.; Zhang, D.; Wang, T.; Zhu, D. *Chem. Commun.* **2003**, 914. (b) Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *J. Org. Chem.* **2003**, *68*, 5681. (c) Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *Chem. Phys. Lett.* **2003**, *375*, 484. (d) Guo, X.; Zhang, D.; Shuai, Z.; Zhu, D. *J. Phys. Chem. B* **2004**, *108*, 212. (e) Guo, X.; Zhang, D.; Zhu, D. *Adv. Mater.* **2004**, *16*, 125. (f) Guo, X.; Zhang, D.; Yu, G.; Wan, M.; Li, J.; Liu, Y.; Zhu, D. *Adv. Mater.* **2004**, *16*, 636.

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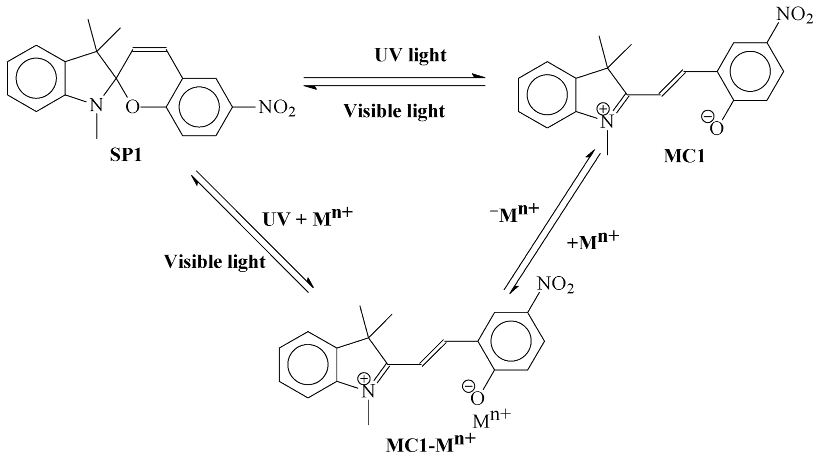
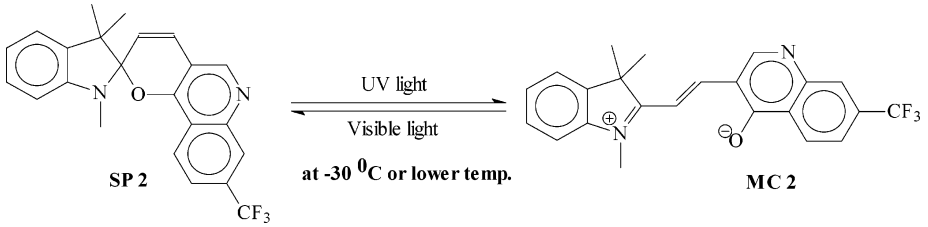
SCHEME 1. Illustrations of the Reversible Structural Transformations of Nitrospiropyran (SP1) in Response to Light, Heat, and Metal Ions



SCHEME 2. Illustration of the Structure and Transformation of SP2/MC2 upon External Stimulations



performed in order to clarify the structures of the colored form of spiropyrans.[9] In addition, the structural information for the metastable species of spiropyrans upon light irradiation has been obtained through stabilization and chemical trapping of these species[3,5,7,10,11] and the combination with crown ether or cyclodextrin.[3a,12] Isolation of the real metastable form of spiropyrans by exposure to UV light or placement in an electrical field in nonpolar or polar solvents was tried,[13,14] but only amorphous powders or quasicrystals of the colored form of spiropyrans were obtained. These studies indicate that the open form of spiropyran owns the hybrid structure between the corresponding zwitterionic and quinoidal ones, and in polar solvents it shows more character of the zwitterionic structure (see Scheme 1) in which the "phenolic" moiety possesses the partial negative charge. It should be emphasized that introduction of electron-withdrawing groups will enhance the stability of the open from of spiropyran. Therefore, one potential approach to stabilize the zwitterionic form of spiropyran is to introduce electron-withdrawing substituents (e.g., nitro-) into the benzene ring that directly fused with pyran ring or substitute the benzene ring with other electron-deficient aromatic groups such as pyridine and quinoline as well as the *N*-methylpyridinium and quinolinium.[15−17] Winkler et al.[15a] once reported that the predominant form of spiropyran with nitroquinoline is the open zwitterionic form in polar solvents. In this paper, we report the synthesis, spectral studies, and theoretical studies of a new spiropyran molecule with a 7-trifluoromethylquinoline group (**SP2**, Scheme 2). The results show that the open zwitterionic form of **SP2** (**MC2**, Scheme 2) is stable both in solution and in the solid state at room temperature. The crystal structure of **MC2** will be described. Spectral studies of **SP2/MC2** in the presence of different metal ions will be also discussed, and the results show its potential in application in sensing metal ions.

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[8] (a) Aramaki, S.; Atkinson, G. H. *J. Am. Chem. Soc.* **1992**, *114*, 438. (b) Chibisov, A. K.; Görner, H. *J. Phys. Chem. A.* **1997**, *101*, 4305. (c) Aubard, J.; Maurel, F.; Buntinx, G.; Guglielmetti, R.; Levi, G. *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 203.

[9] For examples, see: (a) Hirano, M.; Miyashita, A.; Shitara, H.; Nohira, H. *Chem. Lett.* **1991**, 1873. (b) Nakano, S.; Miyashita, A.; Nohira, H. *Chem. Lett.* **1993**, 13. (c) Raic, S.; Vorkapic-Furac, J.; Hergold-Brundic, A.; Nagel, A.; Mintas, M.; Mannschreck, A. *Croat. Chem. Acta* **1996**, *69*, 987. (d) Yagi, S.; Maeda, K.; Nakazumi, H. *J. Mater. Chem.* **1999**, *9*, 2991. (e) Takeda, J.; Ikeda, Y.; Mihara, D.; Kurita, S.; Sawada, A.; Yokoyama, Y. *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 515. (f) Miler-Srenger, E.; Guglielmetti, R. *Acta Crystallogr.* **1982**, *B38*, 1980. (g) Lareginie, P.; Lokshin, V.; Samat, A.; Guglielmetti, R.; Pepe, G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 107.

[10] (a) Suzuki, T.; Lin, F.-T.; Priyadashy, S.; Weber, S. G. *Chem. Commun.* **1998**, 2685. (b) Malatesta, V.; Neri, C.; Wis, M. L.; Montanari, L.; Millini, R. *J. Am. Chem. Soc.* **1997**, *119*, 3451. (c) Malatesta, V.; Milosa, M.; Renzi, F.; Montanari, L.; Wis, M. L.; Scotti, D. *J. Org. Chem.* **1995**, *60*, 5446. (b) Malatesta, V.; Millini, R.; Montanari, L. *J. Am. Chem. Soc.* **1995**, *117*, 6258.

[11] (a) Miyashita, A.; Iwamoto, A.; Kuwayama, T.; Shitara, H.; Aoki, Y.; Hirano, M.; Nohira, H. *Chem. Lett.* **1997**, 965. (b) Winkler, J. D.; Deshayes, K.; Shao, B. *J. Am. Chem. Soc.* **1989**, *111*, 769.

[12] (a) Inouye, M.; Ueno, M.; Kitao, T. *J. Am. Chem. Soc.* **1990**, *112*, 8977. (b) Zhou, J.; Sui, Q.; Huang, B. *J. Photochem. Photobiol. A: Chem.* **1998**, *117*, 129. (c) Kimura, K.; Yamashi, T.; Yokoyama, M. *Chem. Commun.* **1991**, 147. (d) Tanaka, M.; Kamada, K.; Ando, H.; Kitagaki, T.; Shibutani, Y.; Yajima, S.; Sakamoto, H.; Kimura, K. *Chem. Commun.* **1999**, 1453.

[13] (a) Hirano, M.; Osakada, K.; Nohiro, H.; Miyashita, A. *J. Org. Chem.* **2002**, *67*, 533. (b) Krongauz, V. A.; Pershutkin, A. A. *Photochem. Photobiol.* **1972**, *15*, 503. (c) Pershutkin, A. A.; Krongauz, V. A. *Mol. Photochem.* **1974**, *6*, 437. (d) Krongauz, V. A.; Fishman, S. N.; Goldburt, E. S. *J. Phys. Chem.* **1978**, *82*, 2469. (e) Meredith, G. R.; Krongauz, V.; Williamn, D. J. *Chem. Phys. Lett.* **1982**, *87*, 289. (f) Meredith, G. R.; Williams, D. J.; Fishman, S. N.; Goldbert, E. S.; Krongauz, V. A. *Nature* **1984**, *309*, 608. (g) Shvartsman, F. P.; Cabrera, I. R.; Weis, A. L.; Wachtel, E. J.; Krongauz, V. A. *J. Phys. Chem.* **1985**, *89*, 3941.

[14] (a) Heller, C. A.; Fine, D. A.; Henry, R. A. *J. Phys. Chem.* **1961**, *65*, 1908. (b) Onai, Y.; Kasatani, K.; Kobayashi, M.; Shinohara, H.; Sato, H. *Chem. Lett.* **1990**, 1809. (c) Sato, H.; Shinohara, H.; Kobayashi, M.; Kiyokawa, T. *Chem. Lett.* **1991**, 1205.

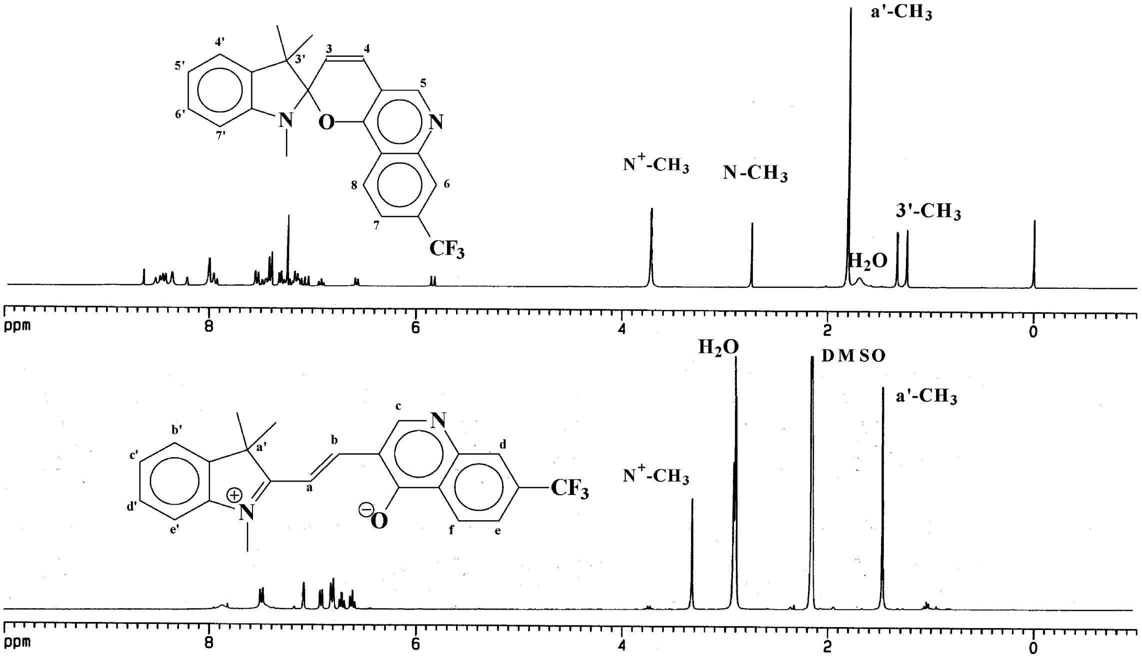
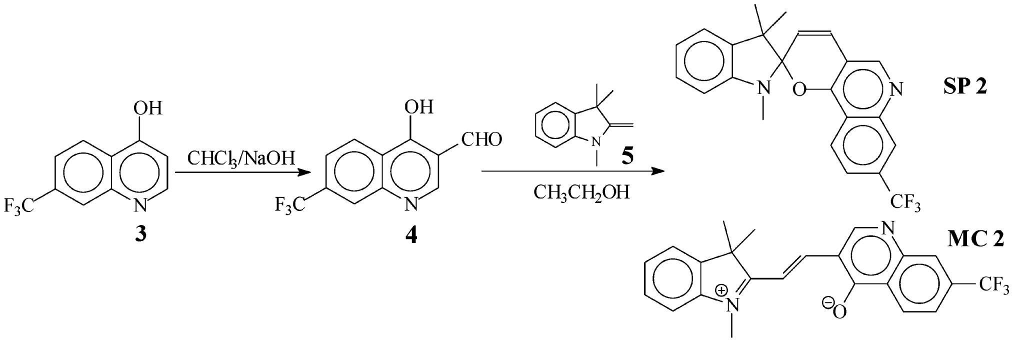


FIGURE 1. ^{1}H NMR spectra for **SP2/MC2** in $CDCl_3$ (top) and DMSO-d_6 (down) at room temperature; the chemical shifts of N^+-CH_3 and a′-CH_3 are high-field shifted in DMSO-d_6 as compared to those in $CDCl_3$.

SCHEME 3. Synthetic Route for SP2/MC2



Results and Discussion

Design and Synthesis. Quinoline-based compounds show interesting fluorescent properties in the presence of metal ions, and consequently, they have been widely investigated as metal-ion sensors, in particular in the biological area.[15] Quinoline can also function as an electron-withdrawing group. In fact, several spiropyrans with quinoline groups were reported by Winkler's group and other groups.[15a,e,16] Among them, the open form of the spiropyran featuring a nitroquinoline group showed the improved thermal stability. In another example, the displacement of the pyridine group with the pyridinium induced the significant shift of the spiropyran ↔ merocyanine equilibrium in THF solution to favor the merocyanine form.[17] These prompt us to further investigate novel quilonine-functionalized fluorescent spiropyrans. Considering these features of quinoline and the fact that trifluoromethyl (CF_3-) is one of the strong electron-withdrawing groups, new spiropyran **SP2** (Scheme 2) was designed for the purpose of gaining the stable merocyanine form in solution as well as in the solid state and providing a potential fluorescent sensor for metal ions.

SP2 was prepared according to the sequence depicted in Scheme 3. Formylation of 7-trifluoromethyl-4-hydroxyquinoline **3** by using the Reimer−Tiemann reaction[18] with chloroform in basic medium led to 7-trifluoromethyl-4-hydroxyl-3-formylquiniline **4** in 16% yield. Condensation of **4** with the Fisher base **5** gave the crude mixture of spiropyran-containing products after refluxing for 4 h in ethanol solution, which was purified by recrystallization from ethanol to afford the pure **SP2/MC2** as purple needles in 57% yield.

^{1}H NMR Spectra and X-ray Crystal Structure. Figure 1 shows the ^{1}H NMR spectrum of the $CDCl_3$ (top) solution of the purple crystals of **SP2/MC2** at room

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[15] For examples, see: (a) Winkler, J. D.; Bowen, C. M.; Michelet, V. *J. Am. Chem. Soc.* **1998**, *120*, 3237. (b) Fahrni, C. J.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 11448. (c) Pearce, D. A.; Jotterand, N.; Carrico, I.; Imperiali, B. *J. Am. Chem. Soc.* **2001**, *123*, 5160. (d) Kimber, M. C.; Mahadevan, I. B.; Lincoln, S. F.; Ward, A. D.; Tiekink, E. R. T. *J. Org. Chem.* **2000**, *65*, 8204. (e) Phillips, J. P.; Mueller, A.; Przystal, F. *J. Am. Chem. Soc.* **1965**, *87*, 4042.

[16] (a) Taylor, L.; Nicholson, J.; Davis, R. *Tetrahedron Lett.* **1967**, 1585. (b) Collins, G. E.; Choi, L.-S.; Ewing, K. J.; Michelet, V.; Bowen, C. M.; Winkler, J. D. *Chem. Commun.* **1999**, 321.

[17] Bénard, S.; Yu, P. *Adv. Mater.* **2000**, *12*, 48.

[18] (a) Jhoer, A.; Denis, G.; Delmas, M.; Gaset, A. *Synth. Commun.* **1988**, *18*, 2095. (b) Bobrański, B. *Ber.* **1936**, *69*, 1113.

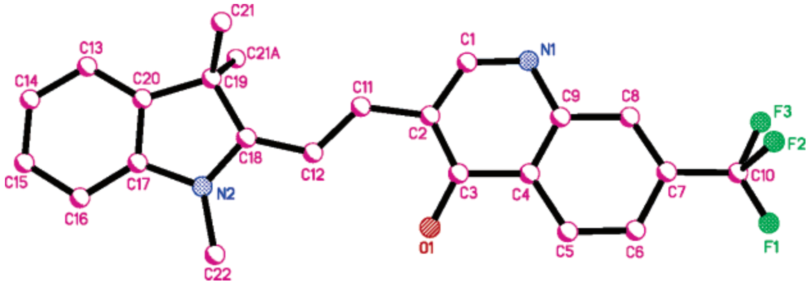

FIGURE 2. Molecular structure of **MC2**; all hydrogen atoms are omitted for clarity.

temperature. For the ^{1}H NMR spectrum of **SP2/MC2** recorded in $CDCl_3$, five signals in the range of 1.00−4.00 ppm are observed. By reference to previous studies, signals at 1.24 and 1.32 ppm are due to two methyl groups at 3′-position of the closed form of **SP2**, which are magnetically not equivalent, and that at 2.76 ppm is ascribed to *N*-methyl group of the closed form of **SP2**. The signals at 1.81 and 3.73 ppm are due to the 3′-methyl and N^+-methyl groups of **MC2** (the open form of **SP2**), respectively. Obviously, the spiropyran (closed form) ⇔ merocyanine (open from) equilibrium exists for the $CDCl_3$ solution of **SP2/MC2** at room temperature (24 °C), and the molar ratio of spiropyran **SP2** vs merocyanine **MC2** is about 0.40 on the basis of this ^{1}H NMR data. The ^{1}H NMR spectra of **SP2/MC2** were also recorded in deuterated solvents of different polarities. As in the case of $CDCl_3$, the spiropyran (closed form) ⇔ merocyanine (open from) equilibrium still exists in CD_2Cl_2, and the molar ratio of **SP2** vs **MC2** is estimated to be 0.42 according to the ^{1}H NMR data (see Figure S2 of the Supporting Information). In DMSO-d_6 solution (bottom, Figure 1), however, only the signals corresponding to **MC2** were detected, and thus only the merocyanine form exists in the DMSO-d_6 solution at room temperature. The same result was obtained in acetone-d_6 and acetonitrile-d_6 as that in DMSO-d_6 (Figure S2 of the Supporting Information). Therefore, it can be concluded that the merocyanine form of **SP2** is stable in solution[19] and the ratio of spiropyran **SP2** vs merocyanine **MC2** is dependent on the polarity of the solvent. In a polar solvent like DMSO, **SP2** exists completely in its open form (merocyanine species). The stability of **MC2** is obviously due to the electron-withdrawing effect of both the quinoline and the trifluoromethyl groups. X-ray crystal structural analysis indicates that **MC2** is also stable in the solid state as discussed below.

Slow evaporation of the solvents from the ethanol solution of **SP2/MC2** at room temperature led to purple crystalline deposits at the bottom of the flask, from which single crystals suitable for X-ray crystallography were selected to determine the crystal structure.[20] Figure 2 displays the molecular structure of **MC2**. The selected bond lengths and angles are provided in the Supporting Information. As illustrated in Figure 2, the crystal is only composed of **MC2**, and the corresponding closed form is not found in the crystal lattice. Except for the trifluoromethyl and two methyl groups (C21 and C21A), all the atoms of **MC2** including C17, C18, C22, and N2 are completely on the same plane, and as a result, the extended π-conjugation along two aromatic moieties (quinoline and indoline rings) is favored. This structural feature may be helpful for the delocalization of the positive and negative charges in **MC2**, which would contribute to the stability of **MC2**. The C3−O1 bond is oriented on the same side of the C22−N2 bond, and hence, the **MC2** has the *s-trans*, *s-cis* conformation. The bond length of C3−O1 is 1.261 (8) Å, which is close to that of a typical C=O bond, indicating that the zwitterion **MC2** in the crystalline state prefers to the quinone structure rather than the phenolate one. The bond lengths of N2−C18 [1.320(8) Å] and C11−C12 [1.371(10) Å] are also close to the corresponding typical double bond lengths, while C12−C18 [1.451(11) Å] and C11−C2 [1.433(11) Å] are relatively longer than these bonds, suggesting bond alteration. The bond lengths of the quinoline ring show the similar bond alternation. Similar crystal data have been very recently described for the open merocyanine form of spirobenzothiopyran,[13a] and in this case the structure is described as extensive zwitterionic form.

In the crystal lattice (Figure S1 of the Supporting Information), the indolinium and the quinoline units of neighboring molecules are arranged in the opposite (heat to tail) way in order to compensate for its dipole moment.[21] In other words, the crystal packing of the zwitterions **MC2** can be basically regarded as H-aggregation[22−24] involving a 2-fold axis in a unit cell. The indolinium moiety and the quinolinium moiety of two

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(19) When the $CDCl_3$ solution of **SP2/MC2** was heated to 40 °C, the molar ratio of **SP2** vs **MC2** was about 0.5, which is comparable to that of the same solution at 24 °C on the basis of the corresponding ^{1}H NMR data (see Figure S3 of the Supporting Information).

(20) Due to the poor quality of the crystals, the precision of the structural data was not satisfactory. But, the correctness of the structure should not be affected. Crystal data: $C_{23}H_{19}F_3N_2O$, M = 396.40, Monoclinic, $P2(1)/m$, a = 11.307(2) Å, b = 6.9899(14) Å, c = 12.560(3) Å, β = 104.97(3)°, V = 959.0(3) Å^3, Z = 2, D_c = 1.373 g cm^{-3}; $F(000)$ = 412, m (Mo K_α) = 0.105 mm^{-1}. Reflections were collected to a q limit of 2.81−27.48° on a Rigaku RAXIS RAPID IP instrument at 173(2) K. The structure was solved by direct methods and refined by a least-squares matrix method. The final cycle of full-matrix least-squares refinement was based on 2224 observed reflections and 176 variable parameters and converged to $R_1 = 0.1100$, $wR_2 = 0.1351$ ($I > 2\sigma(I)$).

(21) Norland, K.; Ames, A.; Taylor, T. *Photogr. Sci. Eng.* **1970**, *14*, 295.

(22) (a) Miyata, A.; Unuma, Y.; Higashigaki, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1719. (b) Uznanski, P. *Synth. Met.* **2000**, *109*, 281. (c) Nakahara, H.; Fukuda, K.; Möbius, D.; Kuhn, H. *J. Phys. Chem.* **1986**, *90*, 6144. (d) West, W.; Pearce, S. *J. Phys. Chem.* **1965**, *69*, 1894.

(23) (a) Ando, E.; J. Miyazaki, J.; Morimoto, K.; Nakahara, H.; Fukuda, K. *Thin Solid Films* **1985**, *133*, 21. (b) Hibino, J.; Hayashida, T.; Suzuki, M.; Kishimoto, Y. *Mol. Cryst. Liq. Cryst.* **1994**, *255*, 243. (c) Kato, K.; Shinbo, K.; Suzuki, M.; Kaneko, F. *Thin Solid Films* **1994**, *243*, 480.

(24) (a) Hirata, Y.; Inoue, T.; Yokoyama, H.; Mizutani, F. *Mol. Cryst. Liq. Cryst.* **1999**, *327*, 249. (b) Tachibana, H.; Yamanaka, Y.; Skai, H.; Abe, M.; Matsumoto, M. *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 149.

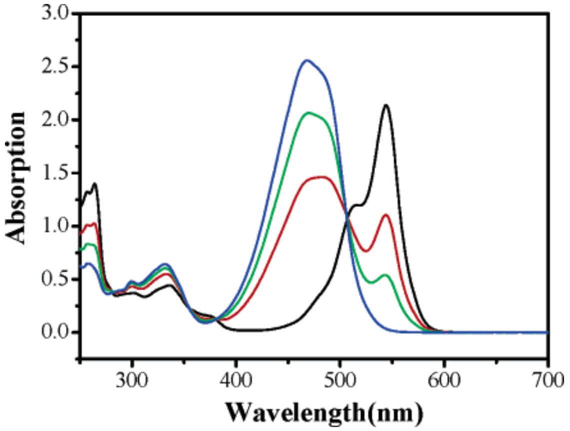

FIGURE 3. Absorption spectrum of **SP2/MC2** (5×10^{-5} M, THF) (black) and those in the presence of 0.5 equiv (red), 1.0 equiv (green), and 2.0 equiv (blue) of CH_3SO_3H.

crystallographically identical molecules are alternately layered over, suggesting the intermolecular dipole interaction between layers.

It should be noted that this is the first report of the crystal structure of the open merocyanine form of spiropyran. The unusual stability of the open form of **SP2** enables us to obtain the crystals which contains completely the open merocyanine form of **SP2**. Efforts were made to obtain the crystals of the closed form of **SP2**, but failed. This is probably due to the stability of the open merocyanine form of **SP2**: evaporation of solvents leads to the precipitation of the open merocyanine form of **SP2**, and hence the concentration of the open merocyanine from of **SP2** in solution will be decreased, simultaneously accompanied with the shift of the spiropyran ⇔ merocyanine equlibrium to favor the open merocyanine form of **SP2**. This process will lead to the complete conversion of the closed form into the open merocyanine form of **SP2**.

Photochromic Property and Theoretical Studies. The needle crystals of **SP2/MC2** can be dissolved in general organic solvents such as THF, chloroform, and toluene, and a deep-red solution is resulted immediately without UV light irradiation. This solution shows strong absorption in the range of 450−600 nm with $\lambda_{max} = 543$ nm (Figure 3), which is the characteristic absorption band of the open merocyanine form of spiropyran. This indicates the presence of the zwitterionic form of **SP2** in solution. This result is in excellent agreement with that of ^1H NMR spectra as discussed above. Addition of CH_3SO_3H to the solution of **SP2/MC2** led to the reduction of the absorption around 543 nm and the appearance of a new absorption band around 450 nm. Accordingly, the color of the solution was changed from red to yellow. This is due to the formation of protonated merocyanine form of **SP2** as for other spiropyrans.[6] If an equivalent amount of triethylamine (vs CH_3SO_3H) was added to the solution of **SP2/MC2** that had been treated with CH_3SO_3H, the typical absorption spectrum of **MC2** was restored.

Usually, the open merocyanine form of spiropyran can be slowly transformed back to the corresponding closed form of spiropyran through thermal relaxation, and the transformation can be accelerated by irradiation with visible light ($\lambda > 460$ nm) at room temperature. However, the conversion of **MC2** to **SP2** did not occur even under visible light irradiation at room temperature. For example, the absorption spectrum of the THF solution of **SP2/MC2** kept unchanged by keeping the solution in the dark for 3 months or even irradiating the solution with visible light ($\lambda > 460$ nm) for 20 h at room temperature. This unusual property is undoubtedly due to the stability of **MC2**.

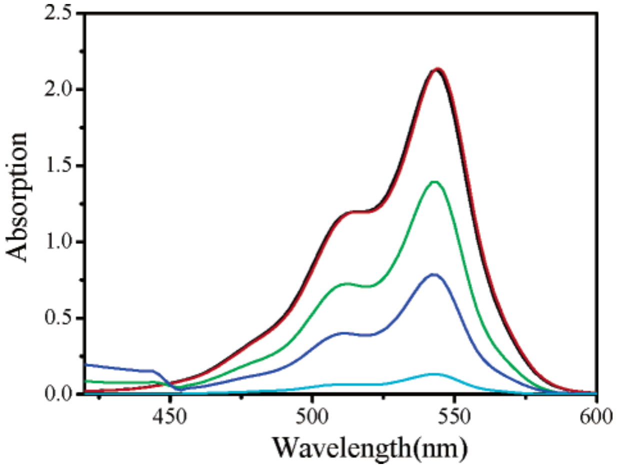

FIGURE 4. Absorption spectrum of **SP2/MC2** (5×10^{-5} M, THF) at 24 °C (black) and those after visible light irradiation for 2 min at 24 °C (red), −30 °C (green), −40 °C (blue), and −50 °C (cyan).

Figure 4 shows the absorption spectra of **SP2/MC2** in THF at −30 °C or lower temperature after visible light irradiation for 2 min.. The results clearly indicate that **MC2** can be transformed into **SP2** under visible light irradiation when the temperature is lowered, although the zwitterion **MC2** does not exhibit photochromism in solution at room temperature. Moreover, it is interesting to note that the colored species of the solution can be slowly converted to the closed form **SP2** at −30 °C or lower temperature in dark. Irradiation with visible light can largely accelerate the conversion of the zwitterion **MC2** to **SP2**. The conversion of **MC2** to **SP2** at low temperature under visible light irradiation was also confirmed by ^1H NMR measurements.[25] On the basis of the corresponding ^1H NMR data, the molar ratio of **SP2** vs **MC2** in $CDCl_3$ was determined to be 0.62, 2.75, and 3.87 for the solution of **SP2/MC2** at −30, −40, and −50 °C, respectively (Figure S3 of the Supporting Information). As for other spiropyran molecules, **SP2** can be transformed to **MC2** under UV light irradiation at low temperature.

To summarize, the transformation of **SP2** to **MC2** cannot proceed through thermal relaxation or under visible light irradiation at room temperature. But, **MC2** shows photochromism by lowering the temperature. To understand this unique property of **SP2/MC2**, theoretical studies were performed. For comparison, the same theoretical calculation was applied to the open and closed forms of 1,3′,3′-trimethyl-6-nitrospiro[(2*H*)-1-benzopyran-2,2′-indoline] (**SP1**, Scheme 1).

The theoretical calculations were performed with the DFT method (see the Experimental Section). The calcu-

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[25] Before recording the ^1H NMR spectra, the $CDCl_3$ solution of **SP2/MC2** was cooled to the temperature at which the measurement would be performed, followed by visible light irradiation for 2 min with a 100 W Tungsten lamp.

TABLE 1. Calculated Thermodynamical Data for SP1→MC1 and SP2→MC2 at 298.15 K and 1 atm

	ΔH (kcal/mol)	ΔG (kcal/mol)	$T\Delta S$ (kcal/mol)
SP2→MC2	−5.00	−7.55	2.34
SP1→MC1	3.31	1.21	2.19

lated thermodynamical data for the transformation of the closed form to the corresponding open form for **SP2** and **SP1** are listed in Table 1. Here, ΔH, ΔG, and ΔS are the corresponding changes of enthalpy, Gibbs free energy, and entropy between the closed and open forms of **SP1** and **SP2**.

The calculation result shows that ΔS for **SP2→MC2** reaction is similar to that for **SP1→MC1** transformation at 298.15 K and 1 atm. But, ΔH for the transformation of **SP2** into **MC2** is negative (Table 1), and as a result the corresponding ΔG (= $\Delta H - \mathrm{T}\Delta S$) is negative, indicating that **MC2** is thermally stable compared with **SP2** and the conversion of **SP2** to **MC2** is thermodynamically favorable. On the contrary, the conversion of the open form to the closed form of **SP2** energetically prohibited. This result is completely in agreement with the experimental results as mentioned above. For the transformation of **SP1** to **MC1**, however, ΔH and ΔG are positive (Table 1). Thus, it can be expected that the conversion of **SP1** to **MC1** is not favorable. But, the reverse reaction can take place from the thermodynamic point. This result is in accordance with the fact that the conversion of **SP1** to **MC1** needs UV light irradiation, and the formed colored species is spontaneously transformed back to the closed form even by keeping the solution in the dark.

The temperature dependence of ΔG can be described by Gibbs−Helmholtz relationship (eq 1). Integral operation with respect to temperature T, under the condition that the variation of ΔH can be neglected, leads to eq 2.

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_{\mathrm{P}} = -\frac{\Delta H}{T^2} \qquad (1)$$

$$\Delta G_2 - \Delta G_1 = \frac{(T_2 - T_1)}{T_1}(\Delta G_1 - \Delta H) \qquad (2)$$

Based on the calculated data in Table 1, $(\Delta G_1 - \Delta H) < 0$ for both **SP1** and **SP2** at 298.15 K (T_1 = 298.15 K). Therefore, when $T_2 > T_1$ (298.15 K), $\Delta G_2 < \Delta G_1$; when $T_2 < T_1$ (298.15 K), $\Delta G_2 > \Delta G_1$. As the ΔG_1 is negative for the reaction **SP2→MC2** at 298.15 K, if the temperature is higher than 298.15 K the transformation of the closed form to the open form of **SP2** will become even more favorable. But, the transformation of **SP2→MC2** will be less thermodynamically favorable if the temperature is lower than 298.15 K. Thus, it is not unexpected that **MC2** can be converted to **SP2** at lower temperature and the process can be accelerated by visible light irradiation. This calculation result provides the explanation for the special photochromic behaviors of **SP2/MC2** as described above. For **SP1→MC1**, however, ΔG_1 is positive at 298.15 K. Thus, the reaction **SP1→MC1** would become thermodynamically favorable by increasing temperature (> 298.15 K), while the reaction becomes thermodynamically even less favorable by lowering the temperature (<298.15 K). This theoretical prediction is consistent with the spectral properties of **SP1** under external stimulations.

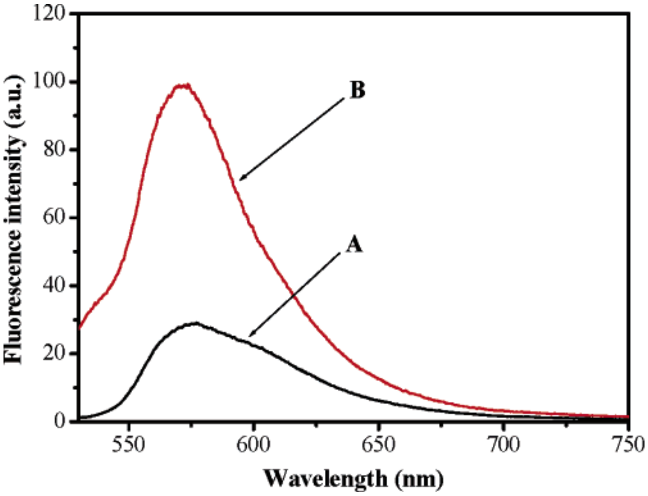

FIGURE 5. Fluorescence spectra of **SP2/MC2** (5×10^{-5} M, THF, at room temperature) excited at 520 nm in the absence of metal ions (A) and in the presence of 10 equiv of $ZnCl_2$ (B).

Spectral Studies of SP2/MC2 in the Presence of Metal Ions. Quinoline and its derivatives are able to form coordination complexes with metal ions, and these metal complexes usually show enhanced luminescent properties. Indeed, quinoline-functionalized spiropyrans were found to be sensitive fluorescent sensors of metal ions. Therefore, it would be interesting to study the absorption and fluorescence spectra of **SP2/MC2** in the presence of metal ions.

As mentioned above, the open merocyanine form of **SP2** is the predominant species in polar solvents at room temperature. Addition of metal ions such as Li^+, Na^+, K^+, Ca^{2+}, Cd^{2+}, Ba^{2+}, and Zn^{2+} to the THF solution of **SP2/MC2** led to the enhancement for the absorption band around 550 nm. But, the corresponding absorption maxima kept almost unchanged. Such absorption increase is very likely due to the shift of the **SP2** ⇔ **MC2** equilibrium to favor the merocyanine species in solution after the weak coordination of **MC2** with these metal ions.

The solution of **SP2/MC2** (5×10^{-5} M in THF) also showed weak fluorescence ($\Phi_F < 0.01$ by reference to 9,10-dibenzoanthracene) with the maximum of the emission band $\lambda_{\max} = 575$ nm upon excitation at 520 nm. This emission should be due to **MC2** according to previous studies.[7b] Interestingly, addition of metal ions such as Zn^{2+}, Ba^{2+}, K^+, and Li^+ to the solution of **SP2/MC2** also results in the fluorescence enhancement. For instance, the fluorescence intensity of the THF solution of **SP2/MC2** at 575 nm increases 3.5 times upon addition of 10 equiv of $ZnCl_2$ as illustrated in Figure 5. The fluorescence enhancement for the solution of **SP2/MC2** after the addition of Li^+, Na^+, K^+, Ca^{2+}, Cd^{2+}, and Ba^{2+} under the same condition (Figure S4 of the Supporting Information) is displayed in Figure 6. It should be noted that the fluorescence spectrum of the solution of **SP2/MC2** shows no obvious hypsochromic shift in the presence of these metal ions, consistent with the corresponding absorption spectra. The observed fluorescence enhancement is probably due to the shift of the spiropyran ⇔ merocyanine

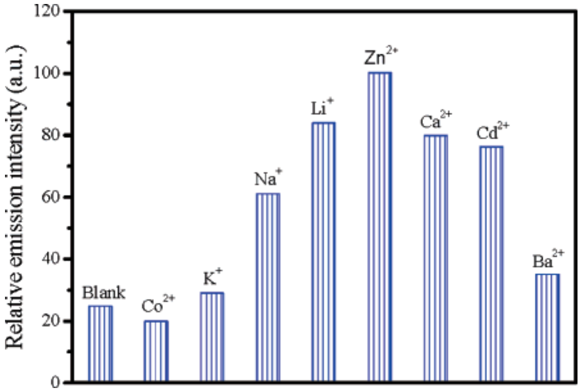

FIGURE 6. Relative emission intensities of **SP2/MC2** at 575 nm (5×10^{-5} M, THF, room temperature) for "metal-free" solutions and those in the presence of 10 equiv of several metal ions (vs **SP2/MC2**).

equilibrium, resulting in the increase of the merocyanine species in solution. Besides, coordination of **MC2** with metal ions may inhibit the photoinduced tautomerization of the hydroxyquinoline moiety which leads to nonradiative deexcitation,[26] thus improving the luminescent property of the quinoline group, based on the results reported previously.[27]

It should be noted that the fluorescence quenching was observed if Co^{2+} was added to the solution of **SP2/MC2** (see Figure 6), resulting from spin−orbit coupling and intersystem crossing due to the proximity of the paramagnetic metal ion to the unpaired electrons of the ligand. Similar effects were found with Ni^{2+}, Fe^{3+}, Cu^{2+}, and Ce^{3+}. However, it is worthwhile to note that these metal ions induced the significant hypsochromic shifts of the fluorescence bands as well as their absorption bands after coordination with **MC2**. As shown in Figure 7, the maximum wavelength of the emission band after complexation of **MC2** with Ni^{2+}, Fe^{3+}, Cu^{2+}, and Ce^{3+} is shifted from the initial value (575 nm) to 525, 531, 538, and 550 nm respectively, while the maximum emission band of **MC2** is shifted to 543 nm in the presence of acid (H^{+}).

Conclusion

A new spiropyran with 7-trifluoromethylquinoline group (**SP2**) was synthesized and characterized. ^{1}H NMR and X-ray structural analysis as well as absorption spectral studies clearly indicate that the open merocyanine form of this new spiropyran (**MC2**) is stable both in solution and in the solid state at room temperature. The stability of **MC2** is obviously due to the electron-withdrawing effect of both the quinoline and the trifluoromethyl groups. Therefore, these results provide a design platform of incorporating the electron-withdrawing groups into the spiropyran molecules for the purpose of fine-tuning the thermal stabilities of their colored open forms.

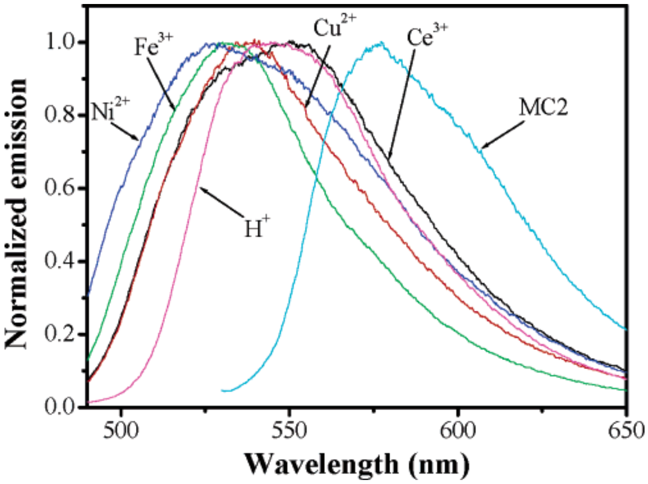

FIGURE 7. Normalized emission spectra of **SP2/MC2** (5×10^{-5} M in THF, room temperature) for "metal-free" solution excited at 520 nm and those in the presence of 10 equiv of paramagnetic ions and proton (vs **SP2/MC2**) excited at 470 nm.

X-ray structural results indicate that except trifluoromethyl and two methyl groups **MC2** is completely planar with *s-trans, s-cis* conformation. It should be emphasized that this is the first report of the X-ray crystal structure of the open merocyanine form of spiropyran. Photochromism of **SP2/MC2** at low temperature is presented, which can be well explained by the thermodynamic data of the theoretical calculation. The spectral properties of **SP2/MC2** in the presence of different metal ions are also studied, and the results show the potential application of **SP2/MC2** in sensing metal ions.

Experimental Section

Computational Methods. The geometric structures of the four compounds, **SP1**, **MC1**, **SP2**, and **MC2** were fully optimized by means of Becke−Lee−Yang−Parr density functional theory (B3LYP-DFT)[28,29] with the 6-31++g(d,p) basis set which includes the polarization and diffusion functions, and using Gaussian03 program package.[30] On the basis of the optimized structures of **SP1 (MC1)** and **SP2 (MC2)**, the vibrational analysis is made for the discussion of their thermodynamical behaviors. The thermodynamical data, such as enthalpy, Gibbs free energy, and entropy, are obtained under the calculation condition of 298.15 K and 1 atm by the vibrational analysis. No imaginary frequencies exist in any of the optimized structures for **SP1**, **MC1**, **SP2**, and **MC2**, which identify them all stable structures at the energy minimum points. The zero-point correction is also considered, but the solvent effect is not included in the calculation.

7-Trifluoromethyl-4-hydroxyl-3-formylquiniline (4). A mixture of 0.30 g of 7-(trifluoromethyl)-4-quinolinol (1.41 mmol), 5 mL of $CHCl_3$, 0.07 g of NaOH, and 50 μL of H_2O was heated to 58 °C for 1 h. A 0.21 g portion of NaOH was added progressively over 2 h at 58 °C. The reaction was allowed to continue for another 1 h. After acidification, the chloroform

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[26] Bardez, E.; Devol, I.; Larrey, B.; Valeur, B. *J. Phys. Chem. B* **1997**, *101*, 7786. For an earlier rationale based on triplet state theory and spin−orbit coupling, see: Popovych, O.; Rogers, L. B. *Spectrochim. Acta* **1959**, 584.

[27] (a) Hercules, D. M.; Rogers, L. B. *Spectrochim. Acta* **1959**, *15*, 393. (b) Popovych, O.; Rogers, L. B. *Spectrochim. Acta* **1960**, *16*, 49. (c) Lytle, F. E.; Storey, D. R.; Juricich, M. E. *Spectrochim. Acta* **1973**, *29A*, 1357. (d) Tian, H.; Qin, B.; Yao, R.; Zhao, X.; Yang, S. *Adv. Mater.* **2003**, *15*, 2104. (e) De Silva, A. P.; McClenaghan, N. D. *Chem. Eur. J.* **2004**, *10*, 574. (f) Ko, C.-C.; Wu, L.-X.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *Chem. Eur. J.* **2004**, *10*, 766.

[28] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

[29] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[30] Frisch, M. J. et al. Gaussian 03, Revision B.02, Gaussian, Inc., Pittsburgh, PA, 2003.

solution was separated. After the solvent was evaporated in vacuo, the residue was further purified by column chromatography on silica gel to yield compound **4** (54 m g, 16%). Mp: 285−286 °C. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 1 H), 8.01 (s, 1 H), 8.34 (d, J = 8.4 Hz, 1 H), 8.70 (s, 1 H), 10.2 (s, 1 H), 12.90 (br, 1 H). MS (EI): *m/z* 241 (M^+). FT-IR (KBr): 1689 cm^{-1} (CHO). Anal. Calcd for $C_{11}H_6NO_2F_3$: H, 2.51; C, 54.76; N, 5.81. Found: H, 2.46; C, 54.60; N, 5.72.

Spiropyran 2. A mixture of 0.11 mL of 1,3,3-trimethyl-2-methyleneindoline (62.2 mmol) and 0.15 g of compound **4** (62.2 mol) in ethanol (20 mL) was refluxed for 3 h under N_2 atmosphere. After the solution was cooled to room temperature, the pure purple crystals were precipitated to yield spiropyran **2** (0.20 g, 57%). Mp: 290−291 °C. ^{1}H NMR (DMSO-*d*D_6): δ 1.66 (s, 6 H), 4.15 (s, 3 H), 7.29 (t, J = 7.5 Hz, 1 H), 7.37 (t, J = 7.5 Hz, 1 H), 7.51 (d, J = 7.7 Hz, 2 H), 7.63 (d, J = 7.5 Hz, 1 H), 7.80 (s, 1 H), 8.26 (d, J = 7.7 Hz, 3 H) 8.75 (br, 1 H). EI MS: *m/z* 396 (M^+). FT-IR (KBr): 1601 (C=C) cm^{-1}. Anal. Calcd for $C_{23}H_{19}N_2OF_3$: H, 4.83; C, 69.67; N, 7.07. Found: H, 4.83; C, 69.47; N, 6.80.

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Supporting Information Available: General experimental methods; solvents and chemicals; conditions for light irradiation experiments; selected bond lengths and angles as well as the intermolecular arrangements in the crystal lattice of **MC2**; ^{1}H NMR spectra of **SP2/MC2** in CD_2Cl_2, acetone-d_6 and acetonitrile--d_3; ^{1}H NMR spectra of **SP2/MC2** in $CDCl_3$ at −30, −40, −50, and +40 °C; fluorescence spectra of the THF solution of **SP2/MC2** in the presence of different amounts of Ba^{2+} ions; crystal structure of **MC2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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