Effect of Complexation with Lanthanide Metal Ions on the Photochromism of (1,3,3-Trimethyl-5'-Hydroxy-6'-Formyl-Indoline-Spiro2,2'-[2H]chromene) in Different Media

M. S. Attia,¹ M. M. H. Khalil,^{1,2} M. S. A. Abdel-Mottaleb,^{1,2} M. B. Lukyanova,³
Yu. A. Alekseenko,³ and Boris Lukyanov³

¹ Department of Chemistry, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt

² Photoenergy Center, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt

³ Institute of Physical and Organic Chemistry, Rostov State University, 194/2 Stachka avenue, Rostov-on-Don 344090, Russia

Received 4 August 2005; Accepted 5 January 2006

Complexation of lanthanide ions {Ln(III) ions [Tb(III), Eu(III), or Sm(III)]} with the spiropyran-derived merocyanine obtained in dark and under steady irradiation of indoline spiropyran (1,3,3-trimethyl-5'-hydroxy-6'-formyl-indoline-spiro-2,2'-[2H]chromene) induces a noticeable hypsochromic shift of about 10–110 nm of its visible absorption band concomitant with hypochromic effect and influences its thermal bleaching in the dark. The effect of lanthanide ions and medium on photochromic, spectral-and-kinetic, and luminescence properties of the spiropyran and its complexes in solution and polymer matrix of polymethylmethacrylate (PMMA) is studied. Efficient energy transfer from the spiropyran moiety results in efficient typical luminescence from the Ln(III) ion that becomes more pronounced in polar nonalcoholic solvents and PMMA solid matrix. Moreover, luminescence mappings for pattern recognition analysis have been obtained from which the nature of the solvent and/or the ligand is clearly identified.

Copyright © 2006 M. S. Attia et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

Photochromism is the process of inducing color changes in a medium by incident electromagnetic radiation [1]. While many different compounds have been shown to exhibit photochromism, the class of spiropyrans molecules has been the most extensively studied over the past several decades. Since the discovery of the photochromic reactions of spiropyrans in 1952 by Fisher and Hirshberg [2], researchers in many laboratories have investigated spiropyrans for various profitable applications. Even in the early work, Hirshberg [2] suggested using the phenomena for a “photochemical erasable memory” and efforts in this direction continue today. Many other applications for spiropyran-based photochromic reactions have been investigated including use as filters in displays, in eye-protective laser goggles, and in self-developing photography [3]. More recently, these molecules have been proposed for use in photoswitching of protein activity [3, 4], as chromophores in 3D optical data storage [5], in information processing [6–8], and as a means to photocontrol ion permeation through biological membranes [9].

This paper reports on the studies of the photochemical and kinetic behavior of (1,3,3-trimethyl-5'-hydroxy-6'-formyl-indoline-spiro-2,2'-[2H]chromene) (SP), containing chelating functional group and its lanthanide metal ion complexation ability in stabilizing the colored merocyanine (MC) form. Furthermore, the process of the energy transfer from the spiropyran moiety to the ion is studied. Factors affecting energy transfer in these systems as well as thermal equilibrium between the closed SP and opened MC forms will be investigated to explore the possibility to stabilize the colored MC form towards thermal reversion by complexation with selected lanthanide metal ions in appropriate solvents.

SCHEME 1

SCHEME 2

2. EXPERIMENTAL

The spiropyran (SP) (1,3,3-trimethyl-5'-hydroxy-6'-formyl-indoline-spiro-2,2'-[2H]chromene) was prepared as follows: to a heated solution of 1.66 g (0.01 mole) 2,4-dihydroxy iso phthalaldehyde [10] and 2.74 g (0.01 mole) of 1,2,3,3-tetramethyl-indolenilium perchlorate was dropwise added 1 ml (0.01 M) piperidine. The reaction mixture was refluxed for 5 minutes and cooled to room temperature. The precipitate was filtered and recrystallized from ethanol. M.p. 147 °C. IR spectra, cm^{-1} : $\nu_{\text{C}=\text{C}}$ 1633, 1613; $\nu_{\text{C}-\text{O}}$ 950. NMR spectra (δ , ppm., J (Hz)): 1.15 (3H, s, $(\text{CH}_3)_2$); 1.25 (3H, s, $(\text{CH}_3)_2$); 2.72 (3H, s, N- CH_3); 5.68 (1H, d, $J = 10.5$, 3'-H); 6.34 (1H, d, $J = 8.7$, 8-H); 6.53 (1H, d, $J = 7.8$, 7-H); 6.85 (1H, t, $J = 7.4$, 5-H); 7.08 (1H, d, $J = 7.3$, 4-H); 7.19 (1H, t, $J = 7.6$, 6-H); 7.25 (1H, d, $J = 10.5$, 4'-H); 7.27 (1H, d, $J = 8.4$, 7-H); 9.63 (1H, s, CHO); 11.78 (1H, s, OH). The lanthanide metal nitrates (Aldrich, 99.99%) were used as received. The solutions of complexes were prepared by mixing of metal nitrate (typical concentration: 8×10^{-5} M), with 3×10^{-5} M of spiropyran in different solvents. Pure grade (Aldrich) solvents were used.

Polymethylmethacrylate (PMMA) matrix was prepared by dissolving appropriate amount of PMMA in chloroform (5 gm PMMA/25 ml CHCl_3) at 30 °C with vigorous stirring for 15 minutes then Eu-SP or Tb-SP complexes were incorporated into PMMA matrix at 30 °C under vigorous stirring for 15 minutes, then PMMA thin film was prepared. The thickness of the thin film was measured by a micrometer and it was found to be 0.4 mm.

UV and visible absorption spectra were measured at room temperature in the UV/visible range (200–650 nm) using λ -Helios SP pye-Unicam spectrophotometer.

Apparent association constants of Sm^{3+} , Eu^{3+} , and Tb^{3+} -SP complexes in acetonitrile were calculated by using Benesi-Hildebrand-type plot (1) [11]:

$$\frac{1}{A_{\text{obs}} - A_o} = \frac{1}{A_c - A_o} + \frac{1}{K_{\text{app}}(A_c - A_o)[M]}, \quad (1)$$

where A_o , A_c , A_{obs} , K_{app} , and $[M]$ are the absorbance of the ligand, the absorbance of the complex, the absorbance of the ligand at various concentrations of the metal ion, the formation constant, and the concentration of the metal ion, respectively.

Luminescence spectra were measured in the range (290–750 nm) using Shimadzu RF5301 (PC) spectrofluorophotometer. Luminescence quantum yield values (Φ_L) of the complexes in different solvents were obtained [12] using rhodamine 101 ($\Phi_f^o = 1$ in ethanol) and quinine sulphate ($\Phi_f^o = 0.546$ in 0.5 M H_2SO_4) as references, respectively. For thin film solid samples, the luminescence quantum yield (relative to the standards above) was determined by measuring luminescence spectra (at $\lambda_{\text{ex}} = 380$ nm) of PMMA films, which are placed in a solid sample holder.

The irradiation source was a 150 W Xenon arc lamp (PTI-LPS-220 Photon Technology International) operated at 70 W with a filter of 437 nm. The light intensity was measured using radiometer (IL 1700 International Light).

The kinetic rate parameters were determined where the rate of transformation of SP to MC obeys first-order kinetics and were calculated from (2) [13]:

$$\ln(A_t - A_e) = -k_{\text{obs}}t + \ln(A_o - A_e), \quad (2)$$

where A_t is the absorbance at λ_{max} of the merocyanine form at time t , A_e is the equilibrium absorbance at the λ_{max} attained under dark conditions (taking the absorbance after at least 15 hours in dark) and A_o is the absorbance at λ_{max} at time zero.

3. RESULT AND DISCUSSION

3.1. Ground state equilibrium

The physical properties of 1,3,3-trimethyl-5'-hydroxy-6'-formyl-indoline-spiro-2,2'-[2H]chromene in solution are determined by the ground state equilibrium, Scheme 2, between the SP form and the trans-merocyanine [14–19]. The absorption spectrum of the compound in acetonitrile has two broad bands in the UV at $\lambda_{\text{SP}} = 255$ nm ($\epsilon = 34100 \text{ M}^{-1}\text{cm}^{-1}$) and at $\lambda_{\text{MC}} = 520$ nm ($\epsilon = 5131 \text{ M}^{-1}\text{cm}^{-1}$) attributed to π - π^* transitions, Figure 1. The equilibrium between both forms is strongly displaced upon irradiation to the side of open-chain colored photomerocyanine and spontaneously converts to the colorless spiroform to reach thermally equilibrated state [20] immediately after removing the light.

The SP-MC equilibrium can be described by the ratio of absorbances at λ_{MC} and λ_{SP} , which is small in all solvents

FIGURE 1: Effect of complexation on the absorption spectra of 3×10^{-5} M of SP: (1) SP in acetonitrile, (2) SP in the presence of 8×10^{-5} M of Eu^{3+} in acetonitrile, (3) 3×10^{-5} M of SP in the presence of 8×10^{-5} M Tb^{3+} in acetonitrile.

TABLE 1: Absorption maxima, ratio of absorbances of SP and trans-MC isomer in different solvents.

Solvent	λ_{MC} (nm)*	$A_{\text{MC}}/A_{\text{SP}}^{\dagger}$
Methanol	504	0.18
Ethanol	522	0.19
Acetonitrile	526	0.21
DMSO	533	0.15
DMF	530	0.44

* λ_{MC} is the maximum wavelength of MC.

$\dagger$ A_{MC} and A_{SP} are absorbance at maximum wavelength of MC and SP, respectively.

except for DMF (Table 1) [21]. This is due to thermal equilibrium between the closed and opened forms which is affected by the change in solvent polarity, since polar solvents promote the formation of the colored form at room temperature in the absence of light, Scheme 2 and Table 1. Figure 1 shows that upon addition of lanthanides (Tb(III) , Eu(III) , or Sm(III)), the absorption band of MC form is blue shifted by (10–110) nm with respect to λ_{MC} indicating that the complex is formed in the ground state (Table 2). This could be due to stabilization of the ground state of MC relative to its excited state, which is noticed to be more pronounced in polar solvents [13, 17]. The blue shift noticed in the presence of rare-earth ions, Figure 1, is larger for the ion with a smallest ionic radius [22]. The formation of the complex is suggested to be due to an equilibrium described in Scheme 3 between the observed solvated complex (termed MC-M^{n+} and S denotes solvent molecules and m = number of molecules) and the MC form. The equilibrium between MC and MC-M^{n+} can be also described by the ratio of absorbances at the two maxima, λ_{com} and λ_{SP} (Table 2). It can be seen from Table 2 that for 3×10^{-5} M of SP and 8×10^{-5} M of metal ions, the $A_{\text{com}}/A_{\text{SP}}$ ratio ranges between 0.3 and 0.93 for (Sm^{3+} , Eu^{3+} , and Tb^{3+}) in methanol and ethanol but ranges between 0.15 and 0.4 in DMSO and DMF. In acetonitrile, the values are higher than 1.0 at $\lambda_{\text{com}}^{\text{max}}$ indicating that a high concentration of the complex in the ground state is favored in polar alcoholic solvents and in acetonitrile. The results clearly show

FIGURE 2: Effect of Tb^{3+} concentration on the absorption spectra of SP in acetonitrile.

FIGURE 3: Effect of Sm^{3+} concentration on the absorption spectra of SP in acetonitrile.

that complexation results in dramatic shift towards MC form [23–27].

More quantitative estimate for complex formation is obtained by applying Benesi-Hildebrand (1). Absorption at 475 nm, as a measure of the complex concentration, increases with the metal ion concentration as shown in Figures 2 and 3. The formation constants of 58×10^3 , 56×10^3 , and $55 \times 10^3 \text{ M}^{-1}$ were obtained for Tb^{3+} , Eu^{3+} , and Sm^{3+} , respectively.

3.2. Effect of irradiation time

Upon UV irradiation, as the irradiation time increased the absorbance of both trans MC and MC-M^{n+} forms is enhanced as well as the luminescence intensity of the complexes, whereas the absorbance of SP form decreases and the thermal relaxation is observed in dark after irradiation. It is well known that the formation and relaxation of the colored form after preirradiation of SP, follows first-order decay kinetics [6, 7, 28, 29]. The life time of the open form

TABLE 2: Absorption maximum of the MC-Mⁿ⁺ complex and the ratio of absorbances of SP form and the complex in different solvents.

Complex	Solvent	λ_{com} (nm) [†]	$A_{\text{com}}/A_{\text{SP}}$ [*]
Sm-MC	Methanol	468	0.93
	Ethanol	417	0.56
	Acetonitrile	389 sh	1.44
		459	2.15
	DMSO	501	0.22
	DMF	510	0.40
Eu-MC	Methanol	486	0.54
	Ethanol	506	0.32
	Acetonitrile	400 sh	
		459	0.76
	DMSO	517	0.16
	DMF	516	0.26
Tb-MC	Methanol	500	0.83
	Ethanol	504	0.24
	Acetonitrile	393 sh	0.56
		459	0.77
	DMSO	520	0.19
	DMF	512	0.40

* A_{com} and A_{SP} are absorbance at maximum wavelength for the complex, SP, respectively.

[†] λ_{com} is the maximum wavelength of the complex.

SCHEME 3

is generally believed to be shorter in lower polarity solvents [30–32]. Moreover, indoline spiropyran and their colored merocyanine forms are separated by the energy barrier [30–32].

In case of reactions that proceed to equilibrium and do not vastly favor the reactant, the concentration (absorbance in this case due to Beer's Law) of reactant follows (2).

k_{obs} in the equation is the sum of the rate constants for the forward and reverse reactions, however, since the thermal ring-opening process is much slower than the ring-closing process [13], $k_{-1} \gg k_1$ and $k_{\text{obs}} \sim k_1$,

The observed rate constants (k_{obs}) for MC and its complexes with (Sm^{3+} , Eu^{3+} , and Tb^{3+}) are calculated from the straight lines of $\ln(A_t - A_e)$ versus time (t). Figure 4 gives an example for k_{obs} calculations.

The calculated k_{obs} in s^{-1} increases in the order $\text{Sm}(1.19) < \text{Eu}(2.01) < \text{Tb}(3.49)$ for the MC-Ln complexes in DMSO.

3.3. Thermal relaxation

It is well known that the MC concentration can be significantly increased upon UV irradiation of SP. After removal of the 70 W light with a filter = 436 nm, the enhancement coloration slowly disappears approaching steady state A_e value at λ_{MC} . The decay is first order and the relaxation time of

TABLE 3: Observed rate constant and relaxation times of MC and its complexes in acetonitrile at 25 °C.

Compound	Observed rate constant (k_{obs}), s^{-1}	k_{-2} , s^{-1}	$\tau_{\text{com-MC}}$, s^{-1}
SP-MC	1.60 (k_1)	0.3 (k_{-1})	3.0
SP-MC Sm	1.19	0.2	5.0
SP-MC Eu	2.01	0.4	2.5
SP-MC Tb	3.49	0.5	2.0

$\tau_{\text{com-SP}}$ = relaxation time of the SP complexes in dark condition.

TABLE 4: Values of the calculated equilibrium constants and the concentration of the complexes at equilibrium conditions at 25 °C.

Compound	Equilibrium constant K_2 , $\text{cm}^3 \text{mol}^{-1}$	$[\text{MC-M}^{n+}]_e \times 10^9 \text{ mol}$
SP-MC Sm	5.95	12.1
SP-MC Eu	5.03	10.2
SP-MC Tb	6.89	13.9

FIGURE 4: $\ln$ scale for 3×10^{-5} M of SP in DMSO. FIGURE 5: Luminescence emission spectra of 8×10^{-5} M of Eu^{3+} in the presence of 3×10^{-5} M of SP in (1) DMSO and (2) acetonitrile. $\lambda_{\text{ex}} = 380 \text{ nm}$.

$\tau_{\text{SP-MC}} = 3 \text{ s}$. The rate constants k_1 and k_{-1} were obtained from $\tau_{\text{SP-MC}}$ and K_1 (Tables 3 and 4). One relaxation time of the complex $\tau_{\text{SP-com}}$ is obtained (for a fixed $[\text{M}^{n+}]$ concentration) from the first-order build up kinetics, i.e. the plots of the linear dependences versus time of $\ln(A_t - A_e)/(A_o - A_e)$, where A_o and A_e denote the initial and final (maximum) values, respectively. The complex concentration under equilibrium conditions and for $[\text{M}^{n+}] \gg [\text{MC-M}^{n+}]$ is given by (4) [33], see Table 4

$$\frac{[\text{MC-M}^{n+}]_e}{[\text{SP}]_o} = \frac{K_1 K_2 [\text{M}^{n+}]_o}{1 + K_1 + K_1 K_2 [\text{M}^{n+}]_o} \quad (4)$$

Here, subscripts e and o refer to the equilibrium and initial concentrations, respectively.

Relaxation time decreases, relative to free MC, in case of Tb and Eu complexes due to strong complex formation. Complexation with samarium induced retardation in relaxation, probably due to a pronounced increase in the formation of MC form as reflected in higher intensity ratios listed in Table 2.

3.4. Medium effect on the luminescence spectra of MC-M^{n+} complexes

Upon excitation of the solution of the complexes of spiropyran with lanthanide ions at $\lambda_{\text{ex}} = 380 \text{ nm}$ the emission spectra show the characteristics bands of the metal ion, Figure 5. The luminescence quantum yields Φ_L for the spiropyrans complexes are low in solution; (DMSO: Tb = 0.056, Eu = 0.052, and Sm = 0.047) due to that luminescence is the only minor deactivation route. A strong increase in Φ_L on going to rigid media (PMMA) (Tb = 0.108 and Eu = 0.085) indicates that other relaxation pathways, in particular rotation around a double bond, are hindered [34], Figures 6 and 7. The calculated quantum yield values of the complexes are listed in Table 5 where the higher values are observed in the less polar solvent (DMF and DMSO) due to the quenching of the emissive excited state in the polar alcoholic solvents (methanol, ethanol, n-propanol, and butanol) [11, 17]. Therefore, with a reduction in the polarity of the solvating medium and changing its nature there is a concomitant reduction in the energy difference between the ground and the excited states [32] and the hydrogen bond formation between the oxygen

TABLE 5: Quantum yields values of (SP-Mⁿ⁺) at $\lambda_{\text{ex}} = 380$ nm.

Solvent	Φ_f SP-Eu $\times 10^{-2}$	Φ_f SP-Sm $\times 10^{-2}$	Φ_f SP-Tb $\times 10^{-2}$
Propanol	0.0	2.7 ± 0.3	3.1 ± 0.2
Butanol	0.0	2.2 ± 0.2	2.2 ± 0.2
Acetonitrile	1.7 ± 0.3	0.8 ± 0.2	1.8 ± 0.2
DMF	2.6 ± 0.4	2.3 ± 0.3	2.8 ± 0.4
DMSO	5.2 ± 0.2	4.7 ± 0.4	5.6 ± 0.2

FIGURE 6: Luminescence emission spectra of 7×10^{-4} M of Tb³⁺ in the presence of 3×10^{-5} M of SP in [PMMA = 8 gm/25 ml] at $\lambda_{\text{ex}} =$ (1) 340 nm, (2) 350 nm, and (3) 380 nm, after two weeks of mixing. FIGURE 7: Luminescence emission spectra of 3×10^{-4} M of Eu³⁺ in the presence of 3×10^{-5} M of SP in [PMMA = 8 gm/25 ml] at $\lambda_{\text{ex}} =$ (1) 340 nm, (2) 350 nm, and (3) 380 nm, after two weeks of mixing.

center and solvating media with hydrogen bond donor capability [30, 35–38]. Furthermore, the luminescence intensity and the quantum yield values of terbium complexes are generally higher than those of europium or samarium complexes in all solvents. The luminescence of Ln³⁺-chelates is related to the efficiency of the intramolecular energy transfer between the triplet level of ligand and the emitting level of the ions, which depends on the energy gap between the two levels. In the organic solvents, the energy gap between the ligand and triplet levels and the emitting level of the terbium favors the energy transfer process for terbium.

FIGURE 8: 3D view of the emission spectra of Eu³⁺ ion in MC-Eu complex at different excitation wavelengths in DMSO.

3.5. Luminescence mapping

Three-dimensional plots of excitation/emission matrix [39, 40] are depicted in Figures 8, 10, and 12. The corresponding tomograms of the two-dimensional representation (luminescence mapping) obtained by connection of data points with the same luminescence intensity (i.e. same height) by lines. Such 2D diagrams always represent a top view [40].

These diagrams seem to be useful as a qualitative tool. In particular, the location and relative intensities of peaks are suitable parameters for pattern recognition analysis as well as a useful analytical method in clinical chemistry and biochemistry [41–44]. The excitation/emission matrix represents the fingerprint of metal ions (Sm, Eu, and Tb ions), and reports on its environment too (Figures 9, 11, and 13).

4. CONCLUSION

Coordinating Ln = Tb(III), Eu(III), or Sm(III), with the open MC form of indoline spiropyran (1,3,3-trimethyl-5'-hydroxy-6'-formyl-indoline-spiro-2,2'-[2H]chromene) takes place thermally (slowly) or photochemically in different solvents and most effectively in DMSO yielding a reversibly photochromic complex. The thermal build-up reaction (s⁻¹) is dependent of Ln(III), which implies that the ring opening is not the rate determining step. Chelation induces a 10–110 nm hypsochromic shift of the visible absorption band of the photomerocyanines. Complexation with Tb(III) and Eu(III) enhances MC thermal bleaching. In case of Sm(III) the thermal bleaching is slowed down possibly due to the

FIGURE 9: Contour view of the emission spectra of Eu^{3+} ion in MC-Eu complex at different excitation wavelengths in DMSO.

FIGURE 12: 3D view of the emission spectra of Tb^{3+} ion in MC-Tb complex at different excitation wavelengths in DMSO.

FIGURE 10: 3D view of the emission spectra of Sm^{3+} ion in MC-Sm complex at different excitation wavelengths in DMSO.

FIGURE 13: Contour view of the emission spectra of Tb^{3+} ion in MC-Tb complex at different excitation wavelengths in DMSO.

FIGURE 11: Contour view of the emission spectra of Sm^{3+} ion in MC-Sm complex at different excitation wavelengths in DMSO.

noticeable shift of the equilibrium towards MC-Sm(III) form. The luminescence quantum yields Φ_L for the spiropyran complexes in PMMA are higher than in solution due to restricted nonradiative dynamical motion in the rigid matrix. Furthermore, luminescence mappings of emissive lanthanides were obtained and can be exploited as fingerprints for analysis.

ACKNOWLEDGMENT

The research of M. S. Attia was supported by the Photoenergy Center, Ain Shams University. The work of the Russian team was supported by Russian Foundation for Basic Research (Grant 04-03-32485) as well as through the Grant CRDF, Ministry of Education of Russian Federation REC-004.

REFERENCES

- [1] H. E. Prysztejn and R. M. Negri, "An experiment on photochromism and kinetics for the undergraduate laboratory," *Journal of Chemical Education*, vol. 78, no. 5, pp. 645–648, 2001.
- [2] E. Fischer and Y. Hirshberg, *Journal of the Chemical Society*, pp. 4522–4524, 1952.
- [3] G. Berkovic, V. Krongauz, and V. Weiss, "Spiropyran and spirooxazines for memories and switches," *Chemical Reviews*, vol. 100, no. 5, pp. 1741–1754, 2000.
- [4] I. Willner, "Photoswitchable biomaterials: en route to opto-bioelectronic systems," *Accounts of Chemical Research*, vol. 30, no. 9, pp. 347–356, 1997.
- [5] S. Kawata and Y. Kawata, "Three-dimensional optical data storage using photochromic materials," *Chemical Reviews*, vol. 100, no. 5, pp. 1777–1788, 2000.
- [6] R. C. Bertelson, "Photochromism," in *Techniques in Chemistry*, G. H. Brown, Ed., vol. 3, pp. 45–294, Wiley-Interscience, New York, NY, USA, 1971.
- [7] R. Guglielmetti, *Photochromism: Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent, vol. 40 of *Studies in Organic Chemistry*, Elsevier, Amsterdam, The Netherlands, 1990.
- [8] J. Malkin, A. S. Dvornikov, K. D. Straub, and P. M. Rentzepis, "Photochemistry of molecular systems for optical 3D storage memory," *Research on Chemical Intermediates*, vol. 19, no. 2, p. 159, 1993.
- [9] R. F. Khairutdinov and J. K. Hurst, "Photocontrol of ion permeation through bilayer membranes using an amphiphilic spiropyran," *Langmuir*, vol. 17, no. 22, pp. 6881–6886, 2001.
- [10] R. Kuhn, *Chemische Berichte*, vol. 87, p. 2876, 1954.
- [11] H. A. Benesi and J. H. Hildebrand, "A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons," *Journal of the American Chemical Society*, vol. 71, no. 8, pp. 2703–2707, 1949.
- [12] J. N. Millar, *Standards in Fluorescence Spectrometry*, Chapman & Hall, New York, NY, USA, 1981.
- [13] J. T. C. Wojtyk, A. Wasey, P. M. Kazmaier, S. Hoz, and E. Buncel, "Thermal reversion mechanism of N-functionalized merocyanines to spiropyran: a solvatochromic, solvatokinetic, and semiempirical study," *The Journal of Physical Chemistry. A*, vol. 104, no. 39, pp. 9046–9055, 2000.
- [14] S.-R. Keum, M.-S. Hur, P. M. Kazmaier, and E. Buncel, *The Canadian Journal of Chemistry*, vol. 86, p. 1940, 1991.
- [15] H. Görner, L. S. Atabekyan, and A. K. Chibisov, "Photoprocesses in spiropyran-derived merocyanines: singlet versus triplet pathway," *Chemical Physics Letters*, vol. 260, no. 1, pp. 59–64, 1996.
- [16] A. K. Chibisov and H. Görner, "Singlet versus triplet photoprocesses in indodicarbocyanine dyes and spiropyran-derived merocyanines," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 105, no. 2–3, pp. 261–267, 1997.
- [17] A. K. Chibisov and H. Görner, "Photoprocesses in spiropyran-derived merocyanines," *The Journal of Physical Chemistry. A*, vol. 101, no. 24, pp. 4305–4312, 1997.
- [18] H. Görner, "Photoprocesses in spiropyran and their merocyanine isomers: effects of temperature and viscosity," *Chemical Physics*, vol. 222, no. 2–3, pp. 315–329, 1997.
- [19] H. Görner, "Photochemical ring opening in nitrospiropyran: triplet pathway and the role of singlet molecular oxygen," *Chemical Physics Letters*, vol. 282, no. 5–6, pp. 381–390, 1998.
- [20] A. Samat, "Thermochromism of organic compounds," in *Organic Photochromic and Thermochromic Compounds*, Vol. 2, chapter 10, Kluwer Academic/Plenum Press, New York, NY, USA, 1999.
- [21] H. Görner and A. K. Chibisov, "Complexes of spiropyran-derived merocyanines with metal ions: thermally activated and light-induced processes," *Journal of the Chemical Society, Faraday Transactions*, vol. 94, no. 17, pp. 2557–2564, 1998.
- [22] Yu. P. Strokach, T. M. Valova, V. A. Barachevsky, V. D. Arsenov, and M. V. Alfimov, *Scientific & Applied Photography*, vol. 42, pp. 531–539, 2001.
- [23] J. Ohno, *Bulletin of the Chemical Society of Japan*, vol. 5, p. 633, 1997.
- [24] M. Le Baccon and R. J. Guglielmetti, *Chemical Research*, vol. 18, p. 1801, 1979.
- [25] L. S. Atabekyan, G. P. Roitman, and A. K. Chibisov, "Complex formation between spiropyran and metal ions in solutions," *Zhurnal Analiticheskoi Khimii*, vol. 37, p. 389, 1982 (Russian).
- [26] L. S. Atabekyan and A. K. Chibisov, "Complex formation of spiropyran with metal cations in solution: a study by laser flash photolysis," *Journal of Photochemistry*, vol. 34, no. 3, pp. 323–331, 1986.
- [27] L. S. Atabekyan and A. K. Chibisov, "Laser photolysis of spiropyran in the presence of metal ions in solutions," *Izvestiya Akademii Nauk SSSR - Seriya Khimicheskaya*, vol. 10, p. 2243, 1988 (Russian).
- [28] A. S. Kholmanskii and K. M. Dyumaev, "The photochemistry and photophysics of spiropyran," *Uspekhi Khimii*, vol. 56, no. 2, pp. 241–266, 1987, English translation in *Russian Chemical Reviews*, vol. 56, no. 2, pp. 136–152.
- [29] T. Bercovici, R. Heiligman-Rim, and E. Fischer, *Molecular Photochemistry*, vol. 1, pp. 23–55, 1969.
- [30] J. B. Flannery Jr., *Journal of the American Chemical Society*, vol. 90, pp. 5660–5671, 1968.
- [31] S. R. Keum, M. S. Hur, P. M. Kazmaier, and E. Buncel, *The Canadian Journal of Chemistry*, vol. 69, p. 1940, 1991.
- [32] X. Song, J. Zhou, Y. Li, and Y. Tang, "Correlations between solvatochromism, Lewis acid-base equilibrium and photochromism of an indoline spiropyran," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 92, no. 1–2, pp. 99–103, 1995.
- [33] A. K. Chibisov and H. Görner, "Complexes of spiropyran-derived merocyanines with metal ions: relaxation kinetics, photochemistry and solvent effects," *Chemical Physics*, vol. 237, no. 3, pp. 425–442, 1998.
- [34] R. C. Bertleson, "Photochromism," in *Techniques of Organic Chemistry*, G. H. Brown, Ed., chapter 3, John Wiley & Sons, New York, NY, USA, 1971.
- [35] J. Arnaud, C. Wippler, and F. Beure D'augeres, *The Journal of Chemical Physics*, vol. 64, p. 1165, 1967.
- [36] H. Takahishi, K. Yoda, H. Isaka, T. Ohzeki, and Y. Sakaino, "Resonance raman studies of transient species in the photochromism of 1',3',3'-trimethylspiro-[2h-1-benzopyran-2,2'-indoline]," *Chemical Physics Letters*, vol. 140, no. 1, pp. 90–94, 1987.
- [37] J. Drummond and D. Neil Furlong, *Journal of the Chemical Society, Faraday Transactions*, vol. 86, p. 3612, 1990.
- [38] A. K. Chibisov, G. V. Zakharova, H. Görner, Yu. A. Sogulyaev, I. L. Mushkalo, and A. I. Tolmachev, "Photorelaxation processes in covalently linked indodicarbocyanine and thiadicarbocyanine dyes," *The Journal of Physical Chemistry*, vol. 99, no. 3, pp. 886–893, 1995.
- [39] O. S. Wolfbeis and M. Leinear, *Analytica Chimica Acta*, vol. 104, p. 203, 1983.

- [40] G. D. Christian, J. B. Callis, and E. R. Davidson, *Modern Luminescence Spectroscopy*, edited by E. L. Wehry, vol. 4, chapter 4, Plenum Press, New York, NY, USA, 1981.
- [41] I. M. Warner, J. B. Callis, E. R. Davidson, and G. D. Christian, "Multicomponent analysis in clinical chemistry by use of rapid scanning fluorescence spectroscopy," *Clinical Chemistry*, vol. 22, no. 9, pp. 1483–1492, 1976.
- [42] R. O. Nodari, S. M. Tsai, R. L. Gilbertson, and P. Gepts, "Towards an integrated linkage map of common bean. II. Development of an RFLP-based linkage map," *Theoretical and Applied Genetics*, vol. 85, pp. 513–520, 1993.
- [43] K. Schumann, A. Baumann, and W. Nagl, "Localization of phaseolin genes in the polytene chromosomes of *Phaseolus coccineus* (Leguminosae)," *Genetica*, vol. 83, pp. 73–76, 1990.
- [44] J. Jiang, B. S. Gill, G. L. Wang, P. C. Ronald, and D. C. Ward, "Metaphase and interphase fluorescence in situ hybridization mapping of the rice genome with bacterial artificial chromosomes," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 92, no. 10, pp. 4487–4491, 1995.