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Substituent effect on the acid-induced isomerization of spiropyran compounds



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1. Introduction

There has been a continuing interest in the isomerization of spiropyran in recent years. Spiropyran compounds are a class of important photochromic compounds, which have a colorless ring-closed "spiropyran" (SP) form that can be converted into the colored open "merocyanine" (MC) form by UV irradiation [1-5]. Furthermore, it also takes place ring opening in the presence of an acid to form protonated merocyanine (MCH) and then converts back to the closed spiropyran form (SP) with the addition of a base [6–10]. In many applications, such as biological probes [11–13], liquid crystals [14], nanoporous conducting particles [15-17], molecular switches [18-22] were designed based on the acid-induced SP-MC isomerization. An advantage of isomerization of spiropyran compounds is the dramatic difference in the photophysical properties of the two isomers, only MC form can emit fluorescence. Acid-induced is beneficial to stabilization of polar MC form and can affect its photophysical properties [23–28]. Exploiting the changes in the photophysical properties of the compounds accompanying their structures will be helpful for the development of the compounds applicable in the fluorescence probes, molecular switches and functional materials.

When suitable substituents were introduced the chromene ring and indole ring of SP (Scheme 1), the transformation from "SP" to "MC" by

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ABSTRACT

Spiropyran compounds are well known as an isomeric system, the closed spiropyran (SP) could be converted into the open merocyanine (MC) via acid-induced because stable protonated merocyanine (MCH) were formed by combination of MC and H⁺. In order to understand how the substituent affect the isomerization of spiropyran. A series of the chromene 7-subsituted spiropyran compounds were designed and synthesized. The photophysical properties of them were studied comparatively by UV-absorption and fluorescence spectra in different pH. The results demonstrated that the various substituents influenced not only the photophysical properties of SP, MC and MCH forms, but also the pK_a of the MC-MCH transformation. There was a good linearity relationship between the pK_a and the Hammett constant of substituent, the pK_a was smaller when the Hammett constant of substituent was larger.

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acidification should be affected and the tunable pK_a values in certain pH range could be achieved. Raymo's group designed a switch based on the chromene 6-nitro substituted spiropyran, the results showed that the electron-withdrawing group enhanced the interconversion between SP and MC states [29]. Chan's group incorporated an oxime moiety [30] and a pH-responsive moiety [31] onto the chromene 8- of the spriopyran, and designed ratiometric pH fluorescence probes based on the excited state intramolecular proton transfer mechanism. Meizhen Yin's group designed the new extreme pH sensors by the introduction of the bulky substituent benzoic acid at the indole N-position and the electron-withdrawing carboxyl group at the indole 6-position of spiropyran [32]. It was clear that the chromene 6-, 8- and indole Nsubsituted spiropyran compounds significantly affect the molecular charge distribution and the process of intramolecular charge transfer of MC state. To the best of our knowledge, less attention has been paid to the chromene 7-position of spiropyran, even less was known how the various substituents with different electron withdrawing or donating power to affects the SP-MC isomerization and the pH range of their control.

In the paper, we designed and synthesized a series of the chromene 7-subsituted spiropyran compounds, the photophysical properties of them were studied comparatively by UV-absorption and fluorescence spectra under pH stimulation. The results showed that pK_a values of the compounds changed gradually accompanying their different substituents (—Cl, —Br, —H, —CH₃, —OCH₃ and —N(CH₂CH₃)₂). As we expected, the chromene 7-substituted spiropyran had a slight adjustment on the pK_a of the MC-MCH transformation. This study opened a new





way to design spiropyran-based fluorescence probes, molecular switches and biological materials.

2. Experiment

2.1. Materials

All chemicals and solvents were analytical grade and were used without further purification. 2,3,3-tetramethyl-3H-indole,ethyl iodide, 4-(dimethylamino)benzaldehyde, 2-hydroxy-4-chlorobenzaldehyde, 2hydroxy-4-bromobenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-4-methylbenzaldehyde and 2-hydroxybenzaldehyde were purchased from the Sigma-Aldrich company. All other chemicals were commercially available from the Beijing chemical reagent company.

2.2. Instruments

All reactions were monitored by thin-layer chromatography on glass plates coated with silica gel GF_{254} (0.25 mm). ¹H NMR and ¹³C NMR spectra were collected on a 400 MHz spectrometer. High-resolution mass spectra were obtained on a Bruker Autoflex mass spectrometer (MALDI-TOF).

UV-absorption spectra were recorded on a Shimadzu UV-265 spectrophotometer (Tokyo, Japan). Fluorescence excitation and emission spectra were measured on a Hitachi F4500 spectrofluorometer (Tokyo, Japan). A PO-120 quartz cuvette (10 mm) was purchased from Shanghai Huamei Experiment Instrument Plants, China. Fluorescence measurements were carried out with excitation and emission slit width of 5 nm.

2.3. Preparation and Characterization of Compound A-F

The synthesis routes of A–F were summarized in Scheme 2. Compound 2(1-Ethyl-2,3,3-trimethyl-3H-indolinium iodide) was synthesized following the literature methods [33]. A mixture of 3.20 g (20.00 mmol) 2,3,3-trimethyl-3H-indinium and 3.58 g (23.00 mmol) ethyl iodide was refluxed in 60 mL of acetonitrile for 24 h. Upon cooling to room temperature, the crude solid precipitated. It was filtered off and washed with ether to give 5.60 g of pink crystals (89%).

1,2,3,3-tetramethyl-3H-indolium iodide (1.88 g, 10 mmol), 4substituted 2-hydroxy-benzaldehyde (10 mmol) and 2.0 mL piperidine were dissolved in 25 mL of CH₃CH₂OH, and the reaction mixture was refluxed with stirring for 12 h and then the solvents were evaporated in reduced pressure. The residue was purified by column chromatography on silica gel to give target compounds. Yield: 45–59%. The structure of A–F fully characterized by ¹H NMR, ¹³C NMR and HRMS-ESI. (see the Fig. S4-Fig. S21).

2.4. General UV-Vis and Fluorescence Spectra Measurements

The stock solutions of the A–F (0.2 mM) were prepared in DMF. And phosphate buffer saline (PBS) buffer was prepared in deionized water. The solutions for spectroscopic determination were prepared by diluting the stock solution with 50 mM buffer (containing 100 mM NaCl for constant ionic strength) at various pH values in a 1 cm quartz cell (totally 3 mL). UV–vis and fluorescence spectra were obtained in DMF: PBS (1: 9 ν/ν , PBS buffer, pH 7.4) solutions. After addition of analytes for 10 min, spectra could be measured. All spectroscopic experiments were carried out at room temperature. The desired solution pH was obtained by addition a certain amount of NaOH (0.1 M) or HCl (0.1 M) to adjust.

3. Results and Discussion

3.1. UV-Vis Absorbance Spectra of Compounds (A-F) in Different pH

In order to know how the different substituents to affect the SP-MC isomerization, six chromene 7-substituted spiropyran compounds (A~F) with different electron withdrawing or donating power (--Cl, -Br, -H, $-CH_3$, $-OCH_3$ and $-N(CH_2CH_3)_2)$ were synthesized. We first investigated their UV-vis absorbance spectroscopic properties in a mixture of DMF: buffer (1: 9, 50 mM PBS buffer) at the concentration of 50 μ M and the detailed experimental data were summarized in Table 1. Fig. 1 showed the UV-vis absorption spectra of compound A under the different pH. From Fig. 1, it was found that compound A exhibited two absorbance bands about 300 and 530 nm at pH = 8.0. With decreasing pH of the solution, the intensity of absorption bands at 300 and 530 nm decreased and a new band was increased at 422 nm, two clear isosbestic points at 320 and 480 nm were observed. When the pH was about 2.0, the absorption bands at 530 and 300 nm disappeared and only a sharp absorption band at 422 nm was observed. The phenomenon was reversible when the pH value was changed from 8.0 to 2.0 and back to 8.0. Meanwhile, the color of the solution changed from purple to shallower, then to yellow accompanying the pH change



I) CH₃CN, reflux, 24h II) Piperidine, EtOH, reflux, 10h

Scheme 2. The synthesis route of compound A-F.

Table	1

Photophysical properties of the spiropyran compounds A-F.

Compound	A (Cl)		B (—Br)	С (—Н)	D (CH ₃)	E (OCH ₃)	$F(-N(CH_2CH_3)_2)$
Yield (%)	50		48	52	59	54	45
$\lambda abs (nm)$	422, 530		424, 538	420, 540	438, 550	446, 528	410, 550
Isosbestic point (nm)	480		486	480	504	492	460
$\epsilon (M^{-1} cm^{-1})$	16,560 (422 n	m)	23,212 (424 nm)	12,121 (420 nm)	21,727 (438 nm)	29,848 (446 nm)	19,484 (410 nm)
	4720 (530 nm	1)	8788 (538 nm)	4242 (540 nm)	4030 (550 nm)	17,848 (528 nm)	73,454 (550 nm)
pH range	3.5-5.6		3.8-5.2	4.1-6	4.2-6.1	4.5-6.3	4.9-6.8
pK _a (abs)	4.46		4.42	5.10	5.23	5.42	5.89
λex (nm)	480		475	495	500	490	450
λem (nm)	540, 635		525, 635	532, 640	537, 640	542,600	540, 597
Isoemission point (nm)	615		605	620	617	607	570
Intensities ratio	0.5-2.2		0.5-2.2	0.359-1.2	0.2-1.0	0.18-11.2	1.5-13
Stokes shift (nm)	(pH = 2)	118	101	112	99	96	130
	(pH = 8)	105	97	100	90	72	50
pK_a (em)	4.74		4.55	5.15	5.29	5.52	5.97

from 8.0 to 2.0 (insert in Fig.1). After increasing pH of the solution, the yellow solution turned purple gradually. It was clear that compound A exhibited a highly reversible response to pH.

The Fig. 2 was the plot of the absorption intensity of compound A at 422 nm against the pH of the solutions, affording a pK_a value of 4.46. The value between absorption intensity correlated nicely with the pH values of the solutions ($R^2 = 0.997$). Moreover, the molar absorption coefficient (ε) could be obtained by using Lambert-Beer's law according to Fig. 1. The ε of compound A at 530 nm and 422 nm were $4720 \text{ M}^{-1} \text{ cm}^{-1} (\text{pH} = 8.0) \text{ and } 16,560 \text{ M}^{-1} \text{ cm}^{-1} (\text{pH} = 2.0), \text{ respectively}$ tively. The change of UV-vis absorption spectra attributed to the isomerization of spiropyran compounds. In the UV-vis spectra of compound A, the 300 nm absorption band was assigned to the SP form, the absorption band at 530 nm belonged to the purple open MC form. In the presence of acid, the MC form converted to yellow protonated merocyanine (MCH) form and the corresponding band at 422 nm was appeared. The interconversion of SP, MC and MCH forms were outlined in Scheme 3. There was the equilibrium between MC and MCH in different pH. The molar absorption coefficients of MC and MCH were constant value. The absorption intensity was mainly determined by the concentration of MC and MCH. In fact, Fig.2 expressed the relationship between MCH concentration and pH value.

The UV–vis absorption properties of compounds B—F were investigated and the experimental data were shown in Table 1. The UV–vis absorption spectra of B—F at different pH and non-linear curve fitting were shown in Fig. S1. These results indicated that: 1) The UV–vis



Fig. 1. UV–vis absorption of compound A ($50 \,\mu$ M) at different pH in PBS buffer/DMF (9:1, ν/ν). Inset: The color of the solution changed from yellow to purple with increasing pH. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

absorption of the six compounds presented a similar response to pH, with decreasing pH of the solution, the absorption intensity of MC at 520–550 decreased and the new band of MCH was observed at 410–450 nm. 2) The ε of MCH at 410–450 nm was higher than them of MC at 520–550 nm, because the MCH form was stabler than the MC form. 3) The pH response range and the pK_a of six compounds were different, they may be caused by the different substituents.

3.2. Fluorescence Spectra of Compounds (A-F) in Different pH

The fluorescence emission spectra of the six compounds were investigated under the same condition and the detailed fluorescence data were summarized in Table1. The fluorescent spectra of the compound A excited at 480 nm in various pH from 2.0 to 8.0 were displayed in Fig. 3. At pH = 2.0, compound A exhibited the emission peak at 540 nm. With an increase in pH, its fluorescence intensity at 540 nm was reduced and a new emission band at 635 nm emerged concomitantly. Apparently, the clear isoemission point was apparent at 615 nm, which indicated the fluorescence intensities ratio (F_{635}/F_{540}) increased from 0.5 to 2.2 associated with pH change from 2.0 to 8.0, giving a change of 4-fold enhancement between two plateaus of the pH titration curve. Non-linear curve fitting using Boltzmann equation, on the basis of the plot of fluorescence intensities ratios (F₆₃₅/F₅₄₀) against pH (inset Fig.3), the pK_a of the probe was calculated to be 4.74. The result was similar to the value by absorbance with pH. In essence, the emission bands at 540 and 635 nm could be assigned to the MCH and MC forms, respectively.

The fluorescent spectra of compounds B–F and their non-linear curves fitting at different pH were measured and shown in Table 1 and Fig. S2. For all these materials, It was found that: 1) The fluorescent



Fig. 2. Nonlinear fitting of the UV-vis absorption at 422 nm.



Scheme 3. The interconversion of SP, MC and MCH forms of compound A-F.

emissions of MCH were at 525–545 nm, while the emissions of MC were observed at 600–640 nm. Obviously, MC showed a remarkable long emission wavelength near the NIR fluorescence region. 2) MC and their protonated MCH of six compounds displayed the significantly large Stokes shift about 99–130 and 50–105 nm, respectively. 3) Ratiometric fluorescence signals were exhibited in different pH solutions, especially compound E showed highest sensitivity with a more than 62-fold enhancement in the fluorescence intensity ratio (F_{600}/F_{540}). On the basis of these results, compounds A–F were suitable for the development of new fluorophores.

3.3. Effects of the Substituents on the Color of MC-MCH

The color change was obvious during the reversible conversion process between MC and MCH in different pH. Unsubstituted spiropyran (C) and its 7-substituted derivatives (B, E) with electron withdrawing (—Br) and donating substituent (—OCH₃) were chosen to compare their color change. Fig. 4 showed the color of them (10^{-5} M) in different pH. We found that the color sudden change point of B and E were about at the pH ~5 and ~6, respectively. It was obvious that the corresponding pH value of color sudden change point was B < C < E. The result was agreement with the pK_a value from spectra experimental.



Fig. 3. The fluorescence emission spectra of compound A (50 μ M) at different pH values in PBS buffer/DMF (9:1, ν/ν) with $\lambda_{ex} = 480$ nm. Inset: Plot of the emission intensities ratios (F_{635nm}/F_{540nm}) to pH variation in PBS buffer/DMF (9:1, ν/ν).



Fig. 4. Color change of compounds B, C and E solution with the increase of pH value from 2.0 to 10.0 under daylight. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4. Effects of the Substituents on the pK_a of MC-MCH

The pK_a of compounds A–F were determined from their absorption and fluorescence spectra in solution of varying pH and shown in Table 2. The data of Table 2 revealed that the pK_a was affected by the substituent type. The influence of substituent type on pK_a values was quantified using Hammett equation [34].

$pK_a = pK_a' + \rho \sigma p$

where ρ is the proportionality constant reflecting the sensitivity of pK_a values to the substituent effects, σ_p is Hammett constant of substituents, refers to unsubstituted spiropyran compound. pK_a refers to substituted spiropyran compounds.

The relation between determined pK_a values and Hammett constants was presented in Fig.5 and there was a good linearity relationship between them. As a result, the chromene 7-substituted spiropyran has a slight adjustment on the pK_a of the MC-MCH transformation. The pK_a was smaller when the Hammett constant of substituents was larger.

Moreover, the Henderson-Hasselbalch equation was also used to calculate the pK_a of the MC-MCH transformation and the detailed data were listed in Table S1 and Fig.S3. The calculation results showed that the change regularity of the pK_a of the spiropyran compounds with different substituent was consistent and good linearity relationships between pK_a values and Hammett constants were obtained by two different equations.

4. Conclusion

In summary, a series of the chromene 7-subsituted spiropyran compounds with different electron withdrawing or donating substituent (—Cl, —Br, —H, —CH₃, —OCH₃ and —N(CH₂CH₃)₂) were prepared to investigate the effects of substitution on isomerization of spiropyran. The experimental results showed that: 1) For six compounds, acid-

Table 2 pK_a and σ_p for various spiropyran compounds.

Compound	Substituent	$\sigma_{\rm p}$	pK _a (abs)	pK _a (em)
А	Cl	0.227	4.46	4.74
В	-Br	0.232	4.42	4.55
С	H	0	5.10	5.15
D	CH ₃	-0.17	5.23	5.29
E	-OCH ₃	-0.268	5.42	5.52
F	$-N(CH_2CH_3)_2$	-0.72	5.89	5.97



Fig. 5. Correlation of pK_a with Hammett constant (σ_p) for various substituents (Abs: $y = -1.54 \times + 4.91$, $R^2 = 0.9278$; Em: $y = -1.60 \times + 4.96$, $R^2 = 0.8910$).

induced was beneficial to stabilization of polar MC form because yellow MCH compound were obtained by combination of MC and H⁺. The maximum UV–vis absorption and fluorescence emission wavelength of MCH were blue-shift than that of MC. 2) The color change of synthetic compounds was obvious in different pH, the corresponding pH value of color sudden change point was, electron withdrawing substituted spiropyrans < unsubstituted spiropyran < electron donating substituted spiropyrans. The result was agreement with the pK_a value from spectra experimental. 3) The substituents on 7-chromene of spiropyran had a slight adjustment on the pK_a of the MC-MCH transformation. There was a good linearity relationship between the pK_a and the Hammett constant of substituent.

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Appendix A. Supplementary data

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