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Fluorescence lifetimes and quantum yields of ten rhodamine derivatives: Structural effect on emission mechanism in different solvents

Xian-Fu Zhang^{a,b,*}, Yakui Zhang^a, Limin Liu^a

^a Chemistry Department, Hebei Normal University of Science and Technology, Qinhuangdao 066004, Hebei Province, China

^b MPC Technologies, Hamilton, ON, Canada L8S 3H4

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ABSTRACT

To get consistent data for ten rhodamine dyes, the fluorescence lifetime, fluorescence quantum yield and spectral properties were measured under the same conditions in four typical solvents by using time-correlated single photon counting and steady state fluorometer. The comparable data make it possible to discuss the mechanism that controls the fluorescence properties of the rhodamine dyes. The data showed that the molecular structure and solvent have remarkable effects. The second alkyl and the rigidity of the alkyls on N atoms are the determining factors for fluorescence lifetime and quantum yields, whereas the substitution on phenyls has little influence. The increase of the solvent polarity decreases both the fluorescence lifetime and fluorescence quantum yield. These results support that the intra-molecular photoinduced electron transfer (PET) may occur from the xanthene moiety to the linked phenyl. The rate constant of radiation process, however, shows no dependence on both the chemical structure and solvents but a constant value ($0.21 \times 10^9 \text{ s}^{-1}$). The rate constant of nonradiation process, on the other hand, is varied with both the structure and the solvent used.

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1. Introduction

The excellent fluorescence properties of rhodamine dyes have gain their widespread applications based on fluorescence signaling and encoding techniques [1–3]. Rhodamine is a family of fluorescence dyes with structures shown in Fig. 1. New rhodamine dyes are still being designed and synthesized to meet various needs under different conditions [4,5], although a variety of chemically modified rhodamine dyes are now commercially available. The basic fluorescence properties of some rhodamines have been measured in water and organic solvents [6–22], but the mechanism tuning their fluorescence properties is not fully established [7]. It is difficult to conclude by comparing the data for the different dyes and correlate their structures to emission properties, since the experiments were carried out by different techniques or instruments under various conditions by different authors. This is because these rhodamine derivatives have been developed at different times over last 90 years.

The fluorescence properties also include fluorescence lifetime (τ_f). The τ_f measurement, however, are much less performed since

it needs more expensive equipments, either in the frequency-domain or in the time-domain [time-correlated single photon counting (TCSPC), streak cameras or up-conversion methods]. On the other hand, fluorescence quantum yield (Φ_f), the band shape and position of emission and excitation spectra can usually be provided by a routine fluorospectrometer.

As a key characteristic of fluorophores, fluorescence lifetime has also gained an important application named as FLIM (fluorescent lifetime imaging microscopy) [3], since it provides useful chemical information due to its sensitivity to the local environment. Therefore the fluorescence properties of rhodamines in various heterogeneous systems have attracted the attention of many researchers [23–54]. Fluorescence lifetimes are also useful on a more fundamental level: to better understand the excited state properties of molecules (to calculate the radiation rate constant k_f by Φ_f/τ_f), to compute the rate constant (or distance) of photoinduced electron (energy) transfer from a donor to an acceptor [3].

Our emphasis in this study is to determine the fluorescence lifetimes of often used commercial rhodamine fluorescent dyes (Fig. 1) under the same conditions. For some of them, the fluorescence lifetime data have not been reported. For others, the lifetimes were reported in different solvents under different experimental conditions or using different instruments/methods. To be consistent, hereby we also report their fluorescence quantum yield Φ_f and spectral parameters. These comparable data renders us to discuss

* Corresponding author at: Chemistry Department, Hebei Normal University of Science and Technology, Qinhuangdao 066004, Hebei Province, China. Tel.: +86 13717599325.

E-mail addresses: zhangxianfu@tsinghua.org.cn, zhangxf111@hotmail.com (X.-F. Zhang).

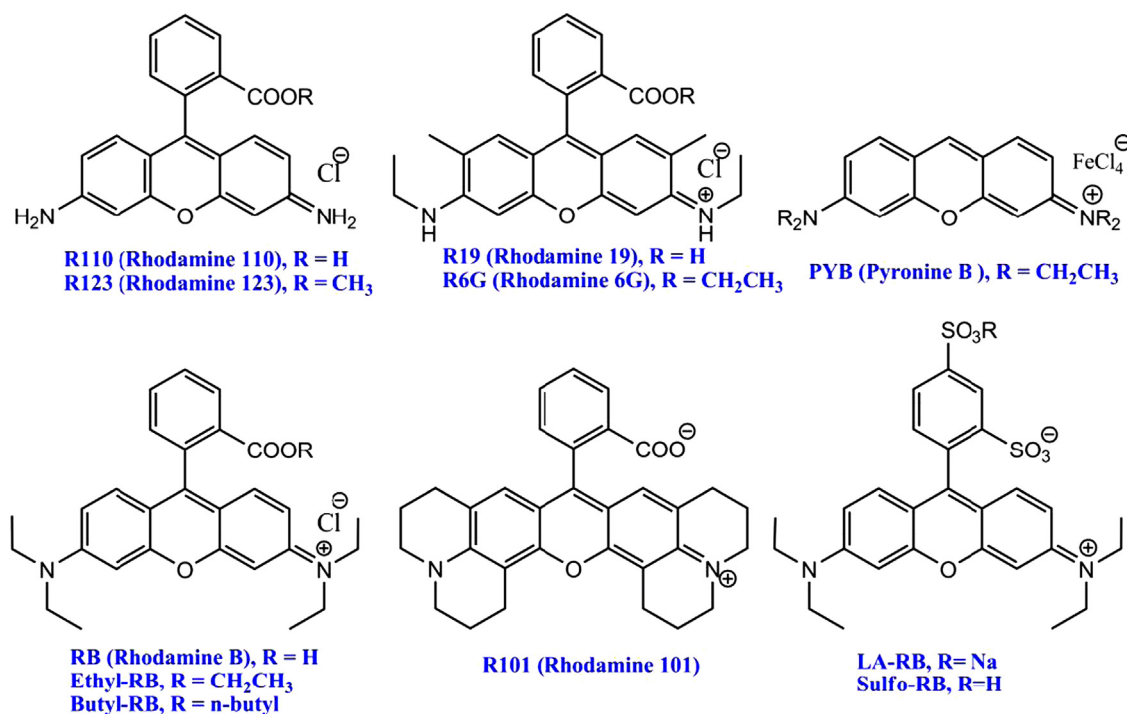


Fig. 1. Chemical structure and abbreviation of rhodamine dyes.

how the structural factors of rhodamine molecules control the fluorescence properties, based on our previous experience in explaining the fluorescence mechanism of fluorescein and its derivatives (also xanthene dyes) [55,56].

2. Materials and solution preparation

The rhodamine dyes in the study (structures are shown in Fig. 1) include Rhodamine 110 (R110), Rhodamine 123 (R123), Rhodamine 19 (R19), Rhodamine 6G (R6G), Rhodamine B (RB), Rhodamine B ethyl ester (Ethyl-RB), Rhodamine B butyl ester (Butyl-RB), Lissamine Rhodamine B (LA-RB), Sulfonyl Rhodamine B (Sulfo-RB), Rhodamine 101 (R101), Pyronine B (PYB). All dyes were purchased with analytical grade or better and used as received. The purity was stated to be better than 97% and only one spot was detectable by TLC. Ethanol, acetonitrile and dimethylformide (DMF) of analytical grade was dried and redistilled immediately before use. Deionized water was purified by Milli-Q system (Millipore, USA).

Acid–base equilibrium exists for some rhodamines that contain PhCOOH in protic solvents, such as RB, R101. To simplify the question, we use the alcohol and water in which 1 mM NaOH was added so that a constant pH was maintained. Under the conditions the protonated (zwitter ion) and lactone form were excluded in protic solvents.

The fluorescence quantum yield is very sensitive to the sample concentration and excitation wavelength due to the self-absorption effect. Therefore the dye concentrations were held low enough to a value yielding an absorbance of ~ 0.020 in a 1 cm path to avoid self-absorption effect. The accurate absorbencies of all the dye solutions were then measured by a 5 cm path length cuvettes on a Hitachi 2450 UV–vis spectrophotometer at the excitation wavelength with a value $0.100 (\pm 0.005)$.

Under the condition in the solvents, the aggregation is negligible. For example, reported values for the dimerization constant of R6G in this solvents lie in the range of $0.11\text{--}6.2\text{ M}^{-1}$ [57]. Accordingly, in our concentration range $0.1\text{--}1\text{ }\mu\text{M}$ for the quantum yield measurements, no aggregates should be formed.

Also the presence of 1 mM NaOH in ethanol consumed protons so that only one emitting species (deprotonated rhodamine) is present in ethanol.

Neither spectral shape nor intensity was changed over time within a week in ethanol, water and acetonitrile. In DMF, however, lactonization occurs with time for RB, Ethyl-RB, Butyl-RB, Sulfo-RB, R101 and R110, therefore the freshly prepared solution was tested immediately against the absorption and fluorescence. The lactone form showed no absorption in the visible region.

3. Methods

Fluorescence measurements were performed by using a FLS 920 fluorospectrometer of Edinburgh Instruments with a 1 cm cuvettes and excitation at 500 nm (20 °C). The emission slit was 1.0 nm while the excitation slit was 0.5 nm. The fluorescence was measured at 90° to the incident excitation beam. The fluorescence intensity at a wavelength was calibrated against the detector response and the excitation light intensity. The fluorescence quantum yield was measured by using

$$\Phi_f = \Phi_f^0 \times \frac{F_s}{F_0} \times \frac{A_0 n_s^2}{A_s n_0^2},$$

in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples. R6G in ethanol was used as the reference ($\Phi_f^0 = 0.95$) [11], since it is esterified and has no deprotonation process. Φ_f values of RB, R6G and R101 thus obtained in ethanol also match the reported values [11,15,16,19–21]. Several measurements for a Φ_f value were performed and averaged by choosing different concentration and excitation wavelength.

Measurements of the fluorescence lifetimes were performed with standard time-correlated single-photon counting method. The exciting light was a portable diode laser (EPL-375, Edinburgh Instruments), the 379 nm (69 ps, 0.10 mW) laser beam was guided into the samples, and fluorescence (the wavelength at the emission maximum of a dye)

Table 1
Photophysical data of rhodamine derivatives in different solvents.

1. Ethanol							2. Water						
	λ_{abs} (nm)	λ_{em} (nm)	Φ_f	τ_f (ns)	χ^2	k_f (10^9 s^{-1})		λ_{abs} (nm)	λ_{em} (nm)	Φ_f	τ_f (ns)	χ^2	k_f (10^9 s^{-1})
Butyl-RB	543	572	0.71	2.92	1.11	0.24	Butyl-RB	558	584	0.30	1.67	1.13	0.18
Ethyl-RB	541	571	0.69	2.94	1.01	0.24	Ethyl-RB	552	581	0.34	1.74	1.10	0.19
LA-RB	552	578	0.68	2.96	1.10	0.23	LA-RB	562	588	0.30	1.49	1.10	0.20
RB	539	571	0.66	2.96	1.00	0.22	RB	554	580	0.36	1.75	1.02	0.20
Sulfo-RB	556	581	0.66	3.00	1.02	0.22	Sulfo-RB	554	591	0.36	1.78	1.07	0.20
R6G	527	552	0.95	3.96	1.02	0.24	R6G	525	554	0.95	4.22	1.05	0.23
R123	506	529	0.88	3.99	1.02	0.22	R123	497	527	0.89	4.20	1.00	0.21
R110	499	525	0.88	4.00	1.08	0.22	R110	497	523	0.85	4.28	1.00	0.20
R101	564	593	0.98	4.74	1.05	0.21	R101	575	604	0.99	4.91	1.00	0.20
PYB	526	557	0.95	3.89	1.15	0.24	PYB	550	555	0.94	4.07	1.13	0.23
3. CH ₃ CN							4. DMF						
	λ_{abs} (nm)	λ_{em} (nm)	Φ_f	τ_f (ns)	χ^2	k_f (10^9 s^{-1})		λ_{abs} (nm)	λ_{em} (nm)	Φ_f	τ_f (ns)	χ^2	k_f (10^9 s^{-1})
Butyl-RB	555	581	0.36	1.61	1.25	0.22	Butyl-RB	562	588	0.35	1.92	1.00	0.18
Ethyl-RB	555	581	0.39	1.69	1.00	0.23	Ethyl-RB	560	585	0.39	2.16	1.19	0.18
LA-RB	548	573	0.52	2.46	1.30	0.21	LA-RB	552	574	0.51	2.84	1.05	0.18
RB	555	579	0.40	1.74	1.23	0.23	RB	560	588	0.42	2.33	1.06	0.18
Sulfo-RB	551	575	0.58	2.47	1.02	0.23	Sulfo-RB	554	576	0.54	2.91	1.18	0.19
R6G	524	552	0.94	4.18	1.00	0.22	R6G	534	562	0.75	3.86	1.00	0.20
R123	500	525	1.00	4.10	1.02	0.24	R123	515	538	0.74	3.74	1.11	0.20
R110	500	523	0.95	4.03	1.00	0.24	R110	515	536	0.87	3.68	1.01	0.24
R101	577	603	1.00	5.25	1.00	0.19	R101	580	608	1.00	4.78	1.08	0.21
PYB	525	549	0.85	4.18	1.05	0.20	PYB	535	562	0.74	3.87	1.05	0.19

was detected with a PMT (Hamamatsu R928) cooled to -21°C . The repetition rate is 10 MHz whilst the count rate did not exceed 20 kHz (0.2%) in order to avoid pile-up effects. The bandwidth for excitation as well as for emission was $< 2 \text{ nm}$. The prompt response function of the system had an fwhm between 500 and 700 ps. The deconvolution method was used to fit the $I(t) = A + B e^{-t/\tau_f}$ to obtain the fluorescence lifetime τ_f .

R6G in ethanol was used as the reference to test the lifetime measurement ($\tau_f = 3.99 \text{ ns}$) [11], which is excellently agreed with the measured value of 3.96 ns. The τ_f values of RB, R6G were also compared with reported values. For example, τ_f of RB was reported to be 2.70 ns in ethanol–water (94:6 v/v) by Snare [20], τ_f for R6G is 3.99 and 3.85 ns in ethanol by Magde and Lopez, respectively [11,58]. These are close to the values obtained in this study.

The fluorescence lifetimes of the dyes showed no dependence on the emission wavelength and sample concentration in the test range from 0.1 to 10 $\mu\text{mol/L}$. The lifetime value of a rhodamine dye was easily reproducible regardless of the change on emission wavelength and the dye concentration.

4. Results and discussion

Table 1 summarizes τ_f values in four solvents found for each rhodamine dye, together with the corresponding Φ_f , emission and absorption maximum (λ_{em} and λ_{abs}) respectively. Among these rhodamines, τ_f and Φ_f of Ethyl-RB, Butyl-RB, and Sulfo-RB have not been reported before, while the data for others were scattered in literature reported in either alcohols or water.

Both τ_f and Φ_f of a dye are of solvent and structure dependence (Fig. 2), and the variation of Φ_f follows the same trend as that of τ_f . The most remarkable observation is that RB and its derivatives (RB, Ethyl-RB, Butyl-RB, LA-RB and Sulfo-RB) all showed close values in τ_f and Φ_f but significantly lower than that of other rhodamine dyes. Importantly, PYB showed remarkably higher τ_f and Φ_f values than RB and its derivatives, although PYB has the same xanthene fluorophores as RB and its derivatives. This indicates phenyl moieties in RB and its derivatives cause the reduction of τ_f and Φ_f values. In the mean time,

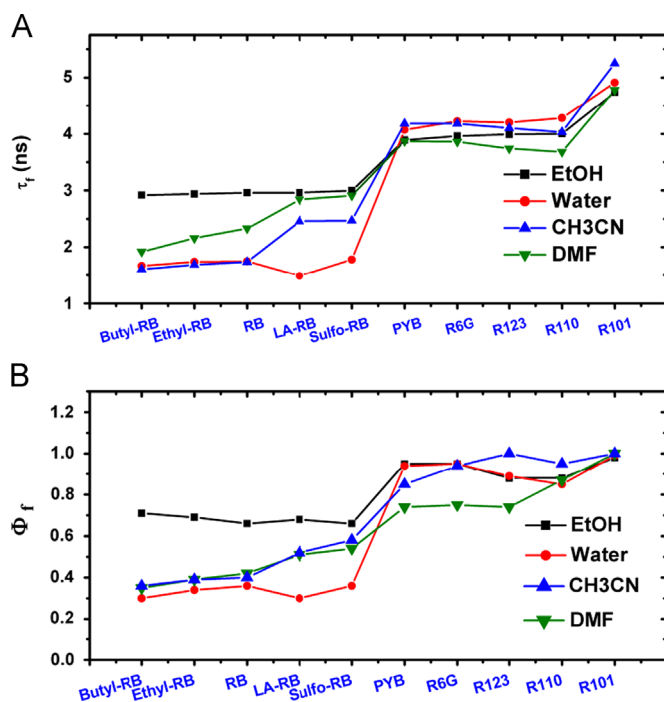


Fig. 2. The change of fluorescence lifetime (A) and quantum yield (B) with the structure and solvent.

phenyl moieties in other rhodamine dyes (excluding RB, Ethyl-RB, Butyl-RB, LA-RB and Sulfo-RB) do not show the behavior. We note, however, the N atoms in other rhodamines have less alkyl than RB and its derivatives. Alkyl carbons in R101 are fixed in a six-member ring, which make R101 have the largest Φ_f and also the longest τ_f . Butyl-RB, on the other hand, exhibited the lowest values in most cases.

The typical emission decay traces are shown in Fig. 3. The convolution analysis generally gave satisfactory mono-exponential results as indicated by the χ^2 value (Table 1). τ_f values for R6G and RB are close to the reported in literature [59]. The typical fluorescence

emission and absorption spectra of the dyes are shown in Fig. 4. The symmetry relation holds between absorption and emission for all the dyes.

Although Φ_f and τ_f are influenced by the chemical structure of a rhodamine dye and the solvent used, their ratio (Φ_f/τ_f) is almost a constant independent of both a dye structure and a solvent. This ratio stands for the rate constant of radiation process ($k_f = \Phi_f/\tau_f$). The average k_f value for all rhodamine dyes is 0.23×10^9 , 0.20×10^9 , 0.22×10^9 , and $0.20 \times 10^9 \text{ s}^{-1}$ for ethanol, water, acetonitrile and DMF respectively.

The absorption and emission maxima, however, are red shifted quite remarkably. The change is about 65 nm from R110 to R101. They are mainly affected by the number and rigidity of alkyl groups on the N atoms (Fig. 5). The red-shift follows this rule:

$$\lambda_{\max}(n=0) < \lambda_{\max}(n=1) < \lambda_{\max}(n=2), \quad n \text{ is the number of alkyls};$$

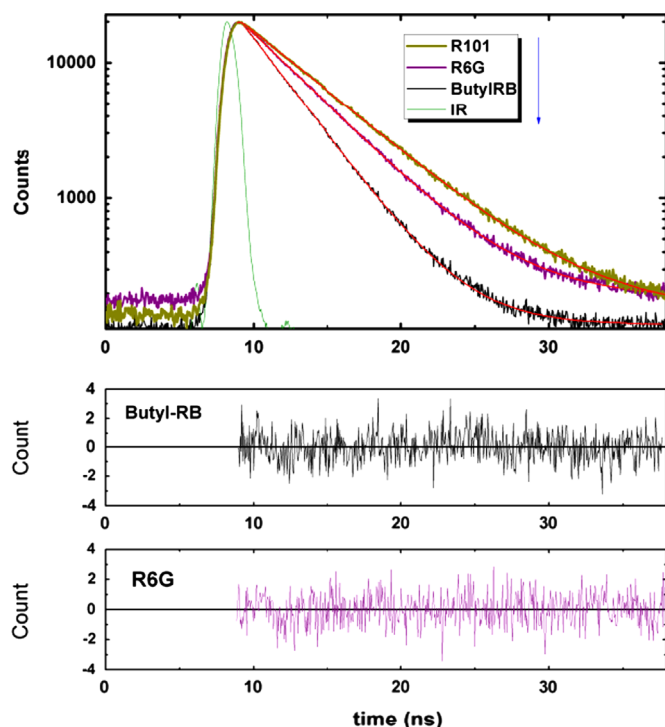


Fig. 3. Fluorescence decay curve, instrument response (IR) curve, fitting line and fitting residue of rhodamines in EtOH containing 1 mM NaOH. Excitation: 379 nm laser (0.1 mW, 69 ps); emission: 590 nm. Chi squared values are listed in Table 1.

$\lambda_{\max}(\text{R}=\text{H}) < \lambda_{\max}(\text{R}=\text{Et}) < \lambda_{\max}(\text{R}=\text{Butyl})$ for COOR on the phenyl;

$\lambda_{\max}(\text{PhCOOR}) < \lambda_{\max}(\text{PhSO}_3\text{R})$;

$\lambda_{\max}(\text{flexible R' on N}) < \lambda_{\max}(\text{rigid R' on N})$.

The rate constant of nonradiative process (k_{nr}) is calculated by $k_{nr} = (1 - \Phi_f)/\tau_f$. In contrast to k_f , the k_{nr} value is varied with both the structure and the solvent. For example, k_{nr} values are 0.40×10^7 , 0.31×10^8 , 0.13×10^8 , $0.12 \times 10^9 \text{ s}^{-1}$ for R101, R110, R6G and RB in ethanol, respectively, which are obviously quite different. The k_{nr} value for RB is 0.11, 0.37, 0.34, and $0.25 \times 10^9 \text{ s}^{-1}$ in ethanol, water, acetonitrile and DMF, respectively.

Ethyl-RB, Butyl RB, Sulfo-RB and LA-RB and RB differ only in their phenyl groups. These five dyes have similar lifetime and quantum yield values in each solvent. For example, τ_f values are $2.96 \pm 0.04 \text{ ns}$ (ethanol) and $1.69 \pm 0.20 \text{ ns}$ (water); Φ_f values are 0.68 ± 0.03 in ethanol and 0.33 ± 0.03 in water. The solvent effect is obvious, the bigger the solvent polarity, the lower the Φ_f , consistent with the presence of PET as discussed in the later section.

Rhodamine B and its derivatives are obtained by substituting 9-H of pyronine B with different benzene moieties (Fig. 1). Comparing the

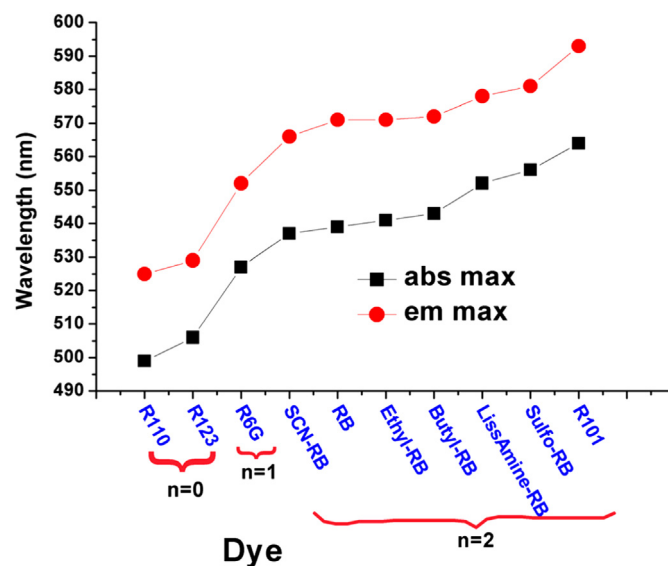


Fig. 5. The effect of n (alkyl number on nitrogen atoms) on the absorption and emission maxima of a rhodamine dye.

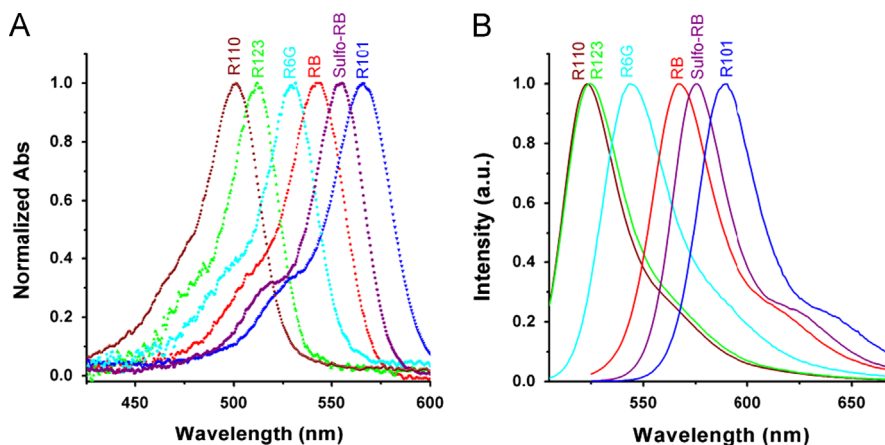


Fig. 4. Typical normalized absorption (A) and emission (B) spectra in ethanol.

data in Table 1 shows that the linkage of a benzene moiety to PYB generally shortens τ_f value by 22–25% and decreases Φ_f by 25–30%.

The phenyl effect in RB and its derivatives is not due to the enhancement of the vibration and rotation which cause the increase of internal conversion (IC) or intersystem crossing (ISC), otherwise the phenyl moiety in R101, R6G and R19 etc. would also have the same effect. In fact the 100% fluorescent efficiency of R101 suggests that the phenyl makes no contribution to the IC or ISC processes that can decrease Φ_f . It is also not caused by chemical reactions, since the fluorescence and UV–vis absorption spectra of these rhodamine dyes are stable in water, ethanol and acetonitrile solvents.

One possible explanation for the phenyl effect is the occurrence of intra-molecular photoinduced electron transfer (PET), which is similar to the case in fluorescein and other xanthene dyes [7,55,56,60,61]. In contrast to other rhodamine dyes, PET is favored in RB and its derivatives due to their dialkylation of N atoms which makes them better electron donors. Also noted is that the solvent effect on Φ_f and τ_f is much more remarkable for RB and its derivatives than that for other rhodamines (Fig. 2). The bigger the solvent polarity, the lower the Φ_f is for RB and its derivatives, consistent with the solvent effect for PET.

The esterification of COOH or replacing COOH by SO₃H in the phenyl of RB has only slight effect on the fluorescence properties of rhodamines. Examine the data for R123 and R110, it shows again that the esterification of COOH on their phenyls shows no effect.

The mono-alkylated R6G have the lifetime comparable to the non-alkylated R123 and R110, all of them have τ_f about 3.98 ± 0.02 ns. So the introduction of the first alkyl onto N atoms has no significant impact.

It is obvious that the presence of second alkyl on N atoms and the rigidity of the alkyl groups are the determining factors for the fluorescence properties, whereas the substitution on the phenyl group has little effect. The rate constant of all these nonradiative photo-physical processes are included in the k_{nr} value. k_{nr} values also strongly correlate to the number and rigidity of alkyl groups on the N atoms.

Two other mechanisms have been proposed to account for the effect of alkyls of rhodamine on its fluorescence properties: (i) pure internal rotation of alkyl groups [62,63]; (ii) a mechanism similar to twisted internal charge transfer (TICT), in which an electron is transferred from the amino group to the xanthene π system to form R₂N⁺–Xanthene^{•–} and the R is rotated about 90° [64].

Mechanism (i) can be excluded, since the substitution of an H atom by an alkyl should decrease the rate of rotation and favors the radiation process, which is converse to the experimental results. Mechanism (ii) proposed that an intramolecular rotational motion towards a low-lying TICT-like state with charge localization proceeds. This mechanism is not related to the phenyl moiety. If it occurs, it must also take effect in the excited R6G and PYB molecules. The 95% emission yield of R6G and PYB indicates that TICT efficiency does not exceed 5%. PET and TICT are not mutually contradictory but can be unified as: R₂N⁺–Xanthene^{•–}–Ph (TICT1) → R₂N⁺–Xanthene–Ph^{•–} (TICT2). The presence of phenyls enhances the TICT2 formation.

TICT state requires a perpendicular mutual orientation between dialkyl amino and the xanthene ring. The presence of the second –CH₂CH₃ increases the electron-donating ability of the N atom (lowers the ionization potentials for different alkylated amines), and enhances the mean ground state twist angle for the amino groups. Both factors favor the TICT-like state and decrease Φ_f and τ_f values. It also illustrates why R101 has a 100% Φ_f . TICT state cannot be formed in R101 due to the steric hindrance.

5. Conclusions

We have measured the fluorescence lifetimes, quantum yields and emission maxima of ten rhodamine dyes and pyronine B

under the same conditions in ethanol, water, acetonitrile and DMF. Based on the data we have discussed the correlation between the rhodamine structures and their fluorescence properties. It has been shown that the presence of the second alkyl and the rigidity of alkyls on N atoms are the determining factors for fluorescence lifetime and quantum yields. The rate constant of radiation process, however, shows no dependence on both the chemical structure and solvents but a constant value (0.21×10^9 s^{–1}). The rate constant of nonradiation process, on the other hand, is varied with both the structure and the solvent used.

The results support the occurrence of intramolecular PET in RB and its derivatives. In this study we have provided a set of consistent fluorescence data for the widely used rhodamine dyes, some of them have not been reported before. We also advance the mechanism study on the fluorescence of rhodamine dyes. The fluorescence data and related emission mechanism are useful for selecting and designing new fluorescent materials and probes needed for different purposes.

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