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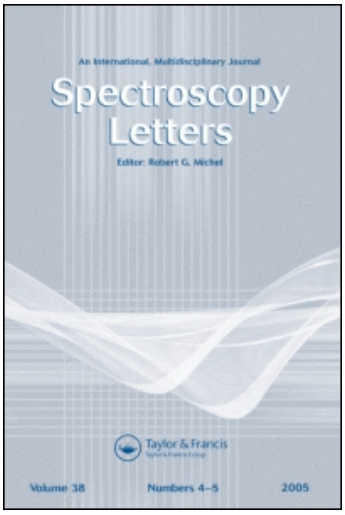

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MOLECULAR STRUCTURE AND PHOTOPHYSICS OF N-QUATERNARY DIARYLOXAZOLIUM SALTS

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MOLECULAR STRUCTURE AND PHOTOPHYSICS OF N-QUATERNARY DIARYLOXAZOLIUM SALTS

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ABSTRACT

The concern of this work is to study molecular structure, electronic absorption and emission spectra of several N-quaternary salts of the well-known diaryloxazole scintillating compounds: 2,5-diphenyloxazole, para-, meta- and ortho-isomers of bis-2-(5-phenyl-oxazolyl)-benzene (POPOP). All of them were obtained from the initial aryloxazoles by their methylation with dimethylsulfate.

We found, that N-methylation manifests itself in arising of sterical hindrance in the molecules of diaryloxazolium salts, which results in distortion of their planarity. On the contrary to the ground state, the investigated molecules become more planar in their lowest singlet excited state. As a result of such an excited state flattening, fluorescence Stokes shifts values of the diaryloxazolium salts exceed 9000–10,000 cm^{-1}.

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The excited state flattening rate constants, estimated for the studied oxazolium compounds, are of the 10^{10} s^{-1} range. No considerable increase of radiationless losses, induced by the excited state structural relaxation, was found. Owing to these facts, N-quaternary diaryloxazolium salts may be considered as effective abnormally high Stokes shift organic luminophores.

Key Words: Diaryloxazole derivatives; N-quaternary salts; Sterical hindrance; Abnormally high fluorescence Stokes shift; Fluorescence quantum yields and lifetimes; Quantum chemical calculations; Excited state structural flattening

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INTRODUCTION

During last years in biologically oriented investigations there was a tendency for usage of organic fluorochromes, which are characterized by high fluorescence quantum yield, emission in the range of higher transmittance of biomaterials, high solubility in water and high binding ability with biopolymers (DNA, proteins).

Among the possible ways for the design of such fluorescent compounds, the most promising seems the structural modification of the already known organic luminophores, for example, N-quaternization of diaryloxazoles, which are widely used in scintillation techniques[1–3]. Introduction of methyl group into the molecules of diaryloxazole series must result in the dramatic increase of their solubility in water and also it must change their spectral properties.

This relatively simple structural modification was made for the first time in late fifties[4,5]. There were also several examples of application of diaryloxazlium salts in fluorescence microscopy and intracellular DNA imaging[6–8]. The double methylated salt of 1,4-bis-2-(5-phenyl-oxazolyl)-benzene (POPOP) was reported as prospective non-intercalative DNA fluorochrome[8]. However, no systematic study of molecular structure and photophysical parameters of diaryloxazolium salts, which are necessary for the better understanding of their behavior in the biological environment, was made till the present time.

In the present paper we study the influence of N-methylation on the molecular structure and spectral properties of several diaryloxazolic compounds, commonly known as effective organic scintillating materials: 2,5-diphenyloxazole **(PPO)**, *para-, meta-* and *ortho*-isomers of bis-2-(5-phenyl-oxazolyl)-benzene **(POPOP)**.

EXPERIMENTAL

Some of the initial diaryloxazolic compounds, **PPO** and **POPOP,** was taken from Aldrich, synthesis of the other ones, *meta*- and *ortho*- isomers of **POPOP** were described in[9,10]. The N-methylated salts were obtained by the following common scheme: 0.1 mL (0.6 mmole) of dimethylsulfate was added to 0.3 mmole of oxazolic compound. Immediate appearance of intensive yellow color indicated starting of interaction. The reaction mixture was heated at 120–125°C during 5 min, cooled to room temperature and dissolved in 2–4 mL of dry methanol. Then dry diethyl ether (5–10 mL) was added and resulted solution was stored during 5–10 hours at $-5 \div 0$°C. Precipitated solid was filtered off and used without additional purification (spectral measurements show absence of even traces of initial oxazolic compounds). Chemical yields were no worse then 80–90%. Melting points of the synthesized N-quaternary salts were near two times higher, than those of initial diaryloxazoles: **Q-PPO** – 150–151°, **Q-*para*-POPOP** – 277–278°, **Q-*meta*-POPOP** – 225–226° and **Q-*ortho*-POPOP** – 195–196°C.

Electronic absorption spectra were recorded on HITACHI U-3210 spectrophotometer, fluorescence spectra – on HITACHI F-4010 fluorescence spectrometer (all the emission spectra were corrected on the spectral response of the instrument).

Fluorescence quantum yields were obtained in respect to quinine sulfate in 1N H_2SO_4 ($\varphi = 0.55$[11]). Time-resolved fluorescence spectra and kinetics were measured on the nanosecond pulse photon-counting spectrometer, described in[12]. Fluorescence kinetics data treatment was made according to[12–14].

Quantum chemical calculations with the optimization of molecular geometry in the ground and in the lowest singlet excited states were made by AM1 method[15] using MOPAC 6.0 program.

RESULTS AND DISCUSSION

To elucidate the influence of N-quaternization of heterocycle(s) to the structure of the formed oxazolium salts, we made quantum chemical calculations with the optimization of molecular geometry by AM1 method. It was revealed, that introduction of methyl group to the nitrogen atom of oxazole cycle results in the arising of sterical hindrance, which causes to the distortion of planarity of the initially flat molecules of **PPO,** ***para*-** and ***meta*-POPOP** (for two last molecules the most energetically favorable conformations have the "opposite" orientation of oxazolium cycles). In all

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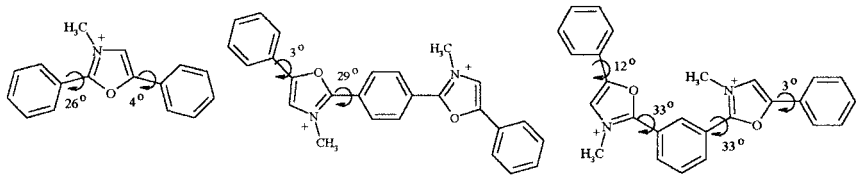
calculated structures benzene ring in the position 2 of oxazolium cycle rotates on the angle of up to 30° due to N-methylation:



Q-PPO **Q-*para*-POPOP** **Q-*meta*-POPOP**

The important question is the stoichiometry of methylation in case of POPOP isomers, which have two oxazole cycles. Authors of the initial synthetic publications[4,5] considered product of POPOP N-methylation as double-quaternized salt. Our model calculations of mono-methylated salts also show high probability of double quaternization: the negative charge on the nitrogen atom of unmethylated oxazole cycle decreases only on 25—30% from the value typical to the initial neutral molecule. Such a decrease in charge corresponds, for example, to the difference between *2,5-diphenyl-1,3-oxazole* and *2,5-diphenyl-1,3,4-oxadiazole* or *isoquinoline* and *quinoline*. These compounds do not differ principally by their basicity and usually they are considered among the strongest organic bases[16]. Thus, nucleophilic capacity of the untouched oxazole cycle in hypothetical mono-quaternized salts of the discussed POPOP isomers may remain quite high to react with the second molecule of dimethylsulfate.

Experimental confirmation of the above conclusion was found at comparison of the absorption spectra of synthesized salts in water with those in concentrated sulfuric acid. Unfortunately, direct comparison of the spectra of mono- and dications of POPOPs in strong mineral acid solutions with the spectra of synthesized salts is hardly probable due to the distortions in planarity caused by methyl groups. Owing to the upper mentioned sterical hindrance, absorption spectra of these salts are shifted towards shorter wavelength spectral region. Also they differ by shape from the spectra of the correspondent protonated mono- and dications. Thus, no more or less grounded conclusion can be made. Our preliminary experiments show the principal possibility to obtain monocationic specimen for the di-basic isomers of POPOP in 5—10% aqueous sulfuric acid solutions, while as 30% of H_2SO_4 is enough to transfer all oxazolic compounds into dications. Thus, if we found no difference in spectra of our N-quaternary salts in water and in 90% acid, we can conclude, that in conditions of our synthesis we obtain doubly quaternized compounds.

According to our AM1 calculations, in the case of non-planar (and also non-symmetrical both in crystalline state[9,10] and in solutions[9,10,12,17])

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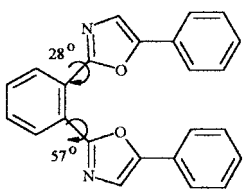
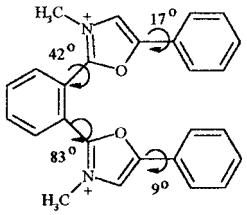
molecule of ***ortho*-POPOP**, introduction of the additional factor of sterical hindrance results in further increasing of inter-cycle angles in the bis-quaternary salt in comparison with the correspondent neutral molecule:



***ortho*-POPOP**



Q-*ortho*-POPOP

Spectral characteristics and fluorescence kinetics data of synthesized quaternary salts are presented in Table 1 for solutions in water and acetonitrile. For the most of compounds it was also possible to obtain qualitative data for chloroformic solutions, in spite of commonly bad solubility in this solvent. As it is clearly seen from the presented results, intensive fluorescence with abnormally high Stokes shift and absence of solvent-induced spectral shifts are typical to all the investigated N-quaternary salts.

Table 1. Spectral Properties of the Investigated Diaryloxazolium N-Quaternary Salts

Compound	Solvent	ν_{abs}, cm^{-1}	ν_{fl}, cm^{-1}	$\Delta\nu_{ST}$, cm^{-1}	φ_{fl}	τ_{fl}, ns	$k_f \cdot 10^{-8}$, s^{-1}	$k_d \cdot 10^{-8}$, s^{-1}
Q-PPO	CH_3CN	33,280	24,140	9140	0.53	1.40	3.75	3.37
	H_2O	33,100	24,000	9100	0.47	1.42	3.30	3.74
	$CHCl_3$	32,640	23,800	8840	—	—	—	—
Q-*para*-POPOP	CH_3CN	28,900	20,680	8220	0.89	2.22	4.02	0.48
	H_2O	28,840	20,740	8100	0.96	2.33	4.10	0.19
	$CHCl_3$	27,580	20,800	6780	—	—	—	—
Q-*meta*-POPOP	CH_3CN	32,420	23,260	9160	0.66	2.76	2.40	1.23
	H_2O	32,120	23,260	8860	0.90	2.84	3.17	0.35
Q-*ortho*-POPOP	CH_3CN	30,660	19,140	11,520	0.82	7.79	1.05	0.23
	H_2O	31,140	18,720	12,420	0.68	7.15	0.95	0.45
	$CHCl_3$	30,160	19,260	10,900	—	—	—	—

Here $_{abs}$ and $_{fl}$ are the positions of the long-wavelength absorption and the emission maxima; Δ_{ST}, φ_f and $_f$ are the fluorescence Stokes shift, quantum yield and lifetime; k_f and k_d are the rate constants of fluorescence emission and radiationless dissipation of the energy of electronic excitation, evaluated from fluorescence quantum yield and lifetime by the well-known formula: $k_f = {}_{fl} \cdot {}_{fl}$, $k_d = (1-{}_{fl}) \cdot {}_{fl}$.

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Two assumptions can be made on the basis of these data. First, the excited state structural relaxation, analogous to that, which was reported by us for the non-planar molecules of ortho-analogs of POPOP [9,10,12,17], might be also typical to the investigated salts. Second, good proximity of the absorption and emission spectra in non-polar $CHCl_3$ and in polar acetonitrile and water may correspond to the relatively small difference in polarity of their molecules in the ground and in the excited states.

Comparison of the spectra of initial diaryloxazoles with those of their N-quaternary salts (Fig. 1) allow us to conclude, that quaternization manifests itself in small hypsochromic shift of the long-wavelength absorption bands. Only one exception was found: positions of first absorption bands of considerably non-planar ortho-POPOP and of its salt were close one to

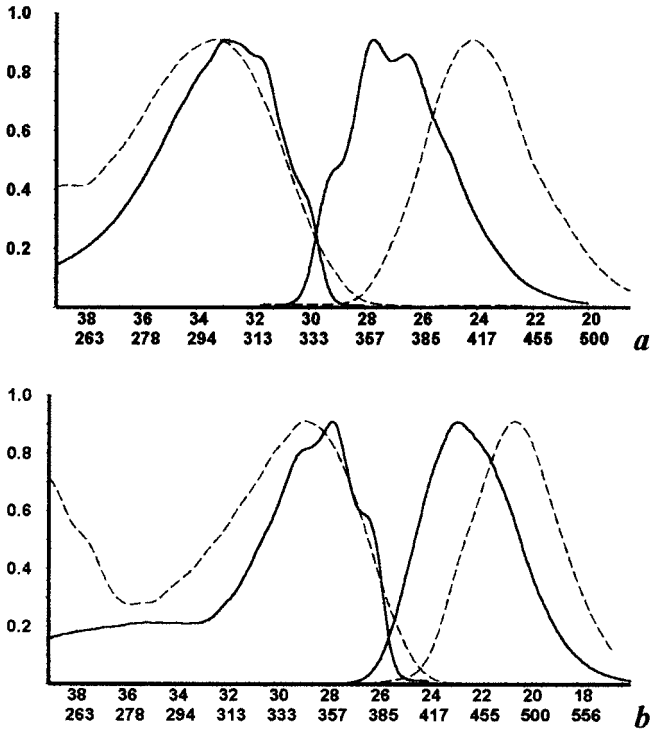

Figure 1. Normalized absorption and emission spectra of diaryloxazoles (solid lines) and their N-quaternary salts (dashed lines) in acetonitrile solutions (in coordinates relative intensity – wavenumber, thous.rev.cm / wavelength, nm): **PPO** and **Q-PPO** (*a*), ***para*-POPOP** and **Q-*para*-POPOP** (*b*), ***meta*-POPOP** and **Q-*meta*-POPOP** (*c*), ***ortho*-POPOP** and **Q-*ortho*-POPOP** (*d*).

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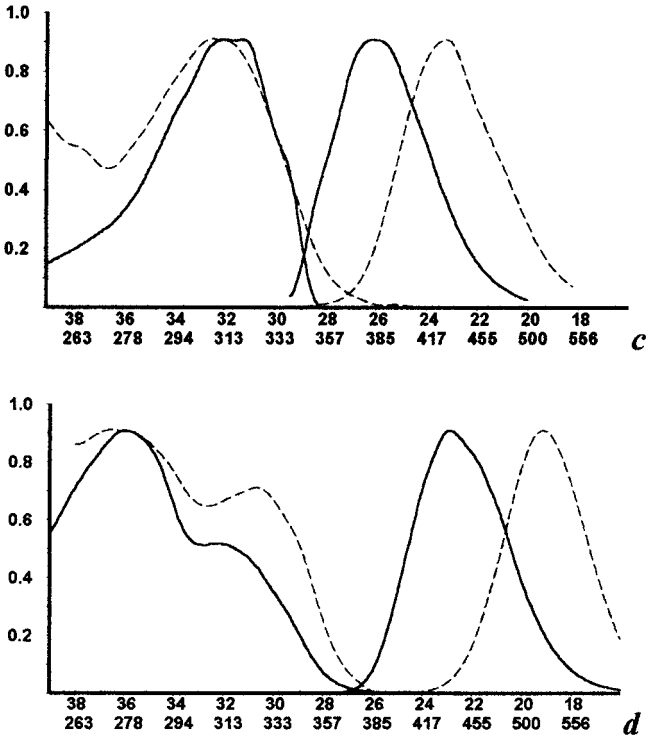

Figure 1. Continued.

another. Among the possible reasons of such behavior we can mention the distortion of planarity of N-methylated molecules. In contrast to the absorption spectra, fluorescence bands of all studied salts are shifted towards longer wavelength compared to the correspondent diaryloxazoles. This fact allows us to assume the possibility of the excited state change in conformation of the investigated N-quaternary salts. Fluorescence quantum yields are high in all examined cases. Definite decrease of fluorescence efficiency was found for **Q-PPO**, though even for this compound quantum yield is no lower than 0.5. Rate constants of radiationless dissipation of the energy of electronic excitation in all cases were equal or lower than the radiative rate constants. Thus, N-quaternary salts of diaryloxazoles display themselves as efficient abnormally high Stokes shift water-soluble organic luminophores.

To elucidate the nature and degree of the excited state structural relaxation we conclude a series of quantum chemical calculations with the

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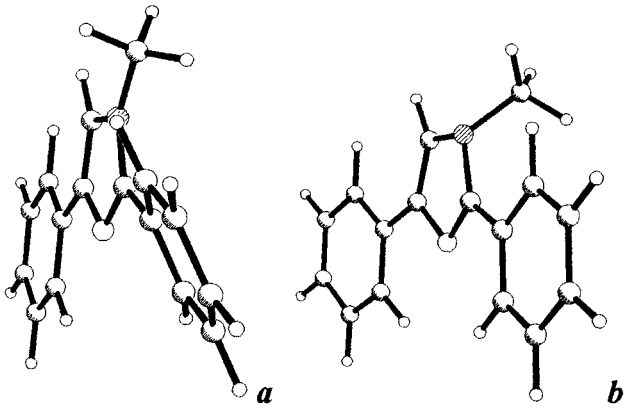

Figure 2. Ground (*a*) and excited state (*b*) molecular structure of **Q-PPO**, AM1 calculations.

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optimization of molecular geometry in S_1^* state by AM1 method. The resulted optimized molecular geometries of **Q-PPO** are presented in Fig. 2. The sp^3-hybrid character of the nitrogen atom of the heterocycle increases in the excited state. This results to the considerable pyramidalization of oxazolium nitrogen atom and to the removal of the methyl group out of the plane of the heterocycle. For this reason, sterical hindrance in the discussed molecule, which caused by N-methylation, decreases in S_1^*-state. The angle between the planes of heterocycle and terminal benzene ring changes from 30 to 5°, so, the excited molecule of **Q-PPO** becomes more planar compared to that in the ground state. Thus, we can conclude, that excited state flattening is typical for the non-planar N-quaternary salts, as well as in the case of previously studied by us non-planar ortho-analogs of POPOP [9,10,12,17].

As it follows from the energetical scheme on Fig. 3a, the mentioned structural changes result in lowering of the energy of structurally-relaxed excited state approximately on $\sim 2500\,cm^{-1}$, while as the energy of correspondent planarized Franc-Condon ground state increases on $\sim 6100\,cm^{-1}$. As a result, the energy of the quanta, emitted by this compound, decrease on $\sim 8600\,cm^{-1}$. This value is close to the experimentally observed fluorescence Stokes shift of **Q-PPO**.

Analogous calculations were made for **Q-*para*-POPOP** (Fig. 3b), and the obtained results were qualitatively the same, as in the case of **Q-PPO**: excited state pyramidalization of its two oxazolium nitrogen atoms and flattening of the molecule as a whole. Moreover, our calculations predicted the certain decrease of Stokes shift of **Q-*para*-POPOP** in comparison with **Q-PPO**, which is observed experimentally (Table 1).

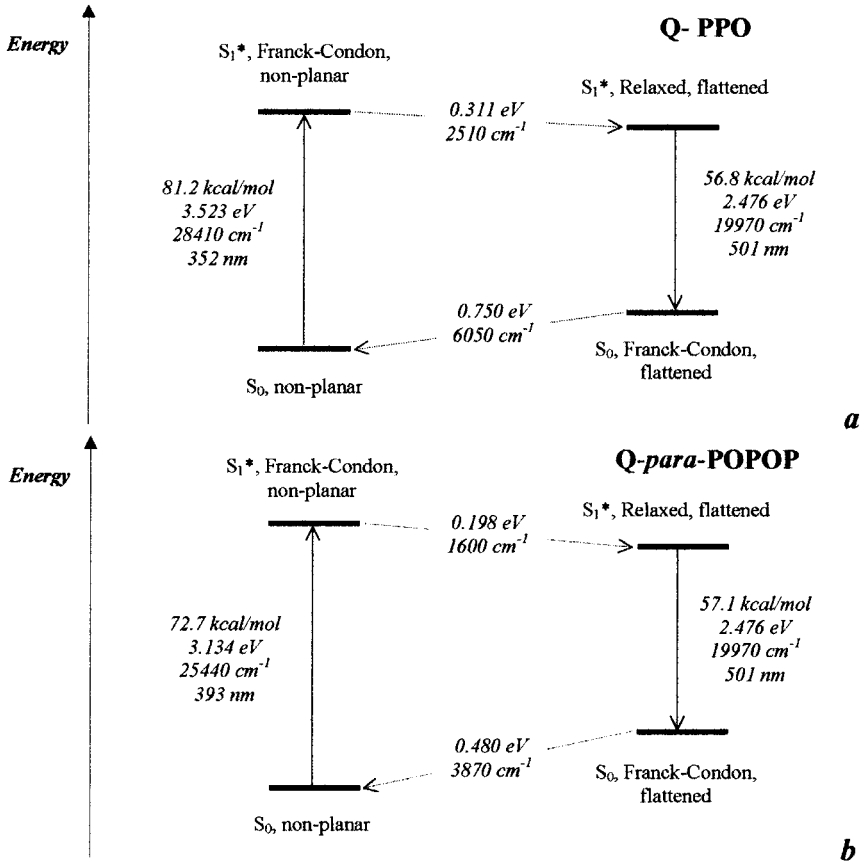

Figure 3. Ground and excited state energetic levels for optimized and Franc-Condon structures of (a) **Q-PPO** and (b) **Q-*para*-POPOP** (AM1 calculation).

The most considerable fluorescence Stokes shifts in the examined series of N-quaternary salts were observed for **Q-*ortho*-POPOP** (11,000–12,000 cm^{-1}). The reason of this might be the interplay of two different relaxation processes in the excited state of this molecule: the flattening typical to the N-quaternary diaryloxazolium salts and the other type of excited state flattening, which is typical to uncharged ortho-analogs of POPOP. In spite of the fact, that S_1^*-state structural relaxation of **Q-*ortho*-POPOP** might be very complicated, we made an attempt to evaluate the rate constant of this process according to[12]. As it was expected, non-exponential decay law and considerable dependence of lifetimes from the

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wavelength of observation, are typical to this molecule. In its time-resolved emission spectra we observed changes, analogous to those of ***ortho*-POPOP**, however long-wavelength shift in the present case was smaller, while as the excited state structural relaxation was faster. The rate constant of **Q-*ortho*-POPOP** excited state flattening was of the order of $1 \cdot 10^{10}$ s^{-1}, while as in the case of correspondent non-quaternary compound the flattening rate constant was near $3 \cdot 10^{9}$ s^{-1} [12,17].

CONCLUSIONS

N-quaternization of polynuclear aromatic derivatives of oxazole results in the increase of sterical hindrance in their molecules. This causes to the disruption of their planarity in the ground state.

The molecules of oxazolium N-quaternary salts become more planar in their lower singlet excited state. This excited state flattening is the reason of abnormally high fluorescence Stokes shifts (up to 10,000 cm^{-1}) typical to the investigated compounds. The most noticeable Stokes shift value (12,000 cm^{-1}) was found for the bis-N-methyl salt of the ortho-POPOP.

The excited state flattening of N-methylated diaryloxazolium salts is a very fast process with the rate constant of the range of 10^{10} s^{-1} and does not result in any considerable reduction of fluorescence quantum yield.

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