

REGULAR ARTICLE

Temperature Effect on the Excited-state Dynamics of 2-Methyl-5-t-butyl-p-quaterphenyl: Three-emission-state mode

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Abstract: The excited-state dynamics of 2-methyl-5-t-butyl-p-quaterphenyl (DMQ) was studied in ethanol at 283–343 K. Results showed that the intensity of steady-state absorption and fluorescence decreased with the increased temperature. Notably, fluorescence lifetime increased with increased temperature, whereas quantum yield increased slowly initially and then decreased quickly. Furthermore, femtosecond time-resolved transient absorption spectroscopy and density functional theory (DFT)/time-dependent DFT were used to interpret the excited-state dynamics of DMQ in ethanol. It showed that the decreased absorption extinction coefficient induced the increase of fluorescence lifetime. And a three-emission-state mode was established to explain the temperature dependence of quantum yield. As a result, the increased population on high energy levels under high temperature enhanced the fluorescence quantum yield of DMQ, but the rotational relaxation and collisional effects induced fluorescence quenching.

AMS subject classifications: 76E07, 92C45

Keywords: rotational relaxation, internal conversion, fluorescence lifetime, transient absorption.

Introduction

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The solvent effect on fluorophore and the solvent environment have a significant effect on the excited-state ultrafast dynamics [1-26]. The solvent environment includes temperature, viscosity, and polarity et al. Recently, the effect of temperature on the kinetics of many organic compounds have been discussed rather extensively in the literatures.[5-8]

Theoretical and general experimental phenomenon showed that the fluorescence lifetime and quantum yield decrease with increased temperature [1-11]. It is due that the collisional and rotational effect enhanced with increased temperature, which caused the fluorescence quenching. It can be interpreted by the well known two-emission-state mode [10]. However, abnormal phenomena were frequently observed in some experiments [12-19]: The fluorescence lifetime and the quantum yield may not decrease with increased temperature, which cannot be understood easily. In 2000, Greiner observed an unusual temperature dependence of the fluorescence quantum yield and lifetime [19]: The fluorescence quantum yield and lifetime pass through a maximum at approximately 180 K when anthracene was dissolved in ethanol. Several models of explanation have been presented to understand the unusual temperature dependences processed [20, 21]. However, the interpretations on the abnormal fluorescence temperature dependence are limited. Such as, Pantke and Labhart proposed a model which assumed constant activation energy but additional transition probability at low energy. This model can simulate a maximum curve; however, no physical evidence or concept was given. [20] Hence, we will focus our attention on the optical transition mechanism to interpret the unusual fluorescence temperature dependence processes.

In this study, we focus our attention on the excited-state dynamics of 2-methyl-5-*t*-butyl-*p*-quaterphenyl (DMQ). **Figure 1** shows the structure of DMQ and the four benzene planes were labeled. DMQ exhibits strong fluorescence in the UV-Vis region, which makes it suitable for using as a colorant. The observation of two-color two-photon excitation fluorescence of DMQ was also reported. [27] However, the environment effect on its excited-state dynamics was seldom reported.

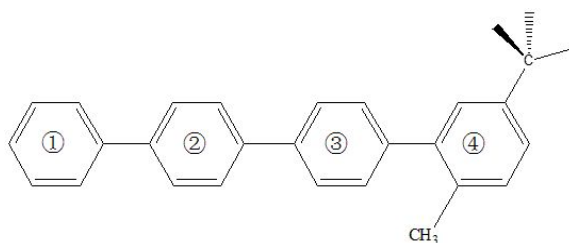


Figure 1: Structure of DMQ, with 1–4 as labels of the four benzene plane.

Herein, the steady-state absorption spectra, fluorescence spectra, fluorescence lifetime, and relative quantum yield of DMQ in ethanol were measured between the temperature

range of 283 and 343 K. Then, the femtosecond pump-probe system was used to observe the transient absorption spectra. The ground-state and first-singlet excited-state of DMQ were investigated using density functional theory (DFT)/time-dependent DFT (TD-DFT). [29] Then, a three-emission-state model will be used to understand the excited-state dynamics of DMQ.

Experimental methods

Steady-state absorption spectra were obtained using the PerkinElmer Lambda 35 double-beam spectrometer. Fluorescence spectra were recorded using the Horiba Jobin Yvon FluoroMax-4P spectrofluorometer. A classical pump-probe setup was used to measure the femtosecond time-resolved transient absorption spectra. [28] Therein, a femtosecond laser system (Spitfire Pro, Spectra-Physic) was used as the light source. The output was 800 nm, with a repetition rate of 1 kHz and a pulse width of <100 fs. The samples were set in a flow cell to prevent photo damage. The samples were detected using their absorption spectra before and after the experiment. No distinct differences in absorption spectra were observed. One Polaroid was placed in the excitation light path. One Berek variable wave plate was placed in the probe light path to adjust the polarization of the probe beam. The polarization of the probe beam with respect to that of the pump beam was adjusted to the magic angle ($\theta = 54.7^\circ$) to prevent the orientation effect. [9,30]

DMQ was purchased from Exciton Inc. and used without further purification. It was dissolved in ethanol to obtain 0.1 mM solutions. A temperature controlled cell holder was used, through which industrial alcohol from a constant-temperature bath was circulated, to control the temperature of the sample cuvette. The temperature in the cuvette could be controlled between 243K and 343K and was monitored directly using a thermocouple.

Computational Method

The ground-state and excited-state were calculated using the Gaussian 09 program. [32] The ground-state geometries of DMQ were optimized using DFT methods. B3LYP functional and 6-31G(d,p) basis sets were used for all calculations. The polarizable continuum model (PCM) was used to consider the solvent effect. The solvent ethanol was considered. The vertical excitation energies and the excited-state optimized geometries of DMQ were calculated using TD-DFT methods. Following each optimization, the vibrational frequencies were computed. We systematically checked that all vibrational frequencies are real.

Results and Discussions

Optimized Structures of DMQ

Given the flexibility of the DMQ structure, two optimized conformers of DMQ in ethanol (A and B; **Figure 2**) were obtained using DFT at ground-state (S_0). These two conformers, A and B, were also optimized using TD-DFT at their first-singlet excited-state (S_1). **Figure 2** shows the four optimized geometries: ground-state of conformer A (A- S_0 -opt), ground-state of conformer B (B- S_0 -opt), optimized excited-state of conformer A (A- S_1 -opt), and optimized excited-state of conformer B (B- S_1 -opt).

Table 1 shows that the optimized geometries of DMQ have some differences between A and B structures, however, the energy are almost the same for both A and B. Considering the structure of S_0 optimized geometries and S_1 optimized geometries, it is obtained that the largest torsion angle from B- S_0 -opt to B- S_1 -opt (64 degree) is larger than the torsion angle from A- S_0 -opt to A- S_1 -opt (34 degree, see **Table 1** and **Figure 2**). As such, it is reasonable to assume that the rotational time from B- S_0 -opt to B- S_1 -opt is longer than the rotational time from A- S_0 -opt to A- S_1 -opt. In addition, **Table 1** shows the four benzene planes are nearly parallel both for A- S_1 -opt and B- S_1 -opt.

Table 1. Characteristic structures of DMQ at the S_0 and S_1 optimized geometries. PCM model was used, and ethanol was considered as solvent.

Geometry	Conformer					E+1,122/(a.u.)
S_0 -opt	A	35.7	1.2	53.8		-0.0389
	B	35.7	71.0	56.4		-0.0389
S_1 -opt	A	12.9	14.6	20.0		0.0846
	B	13.4	7.0	41.3		0.0845

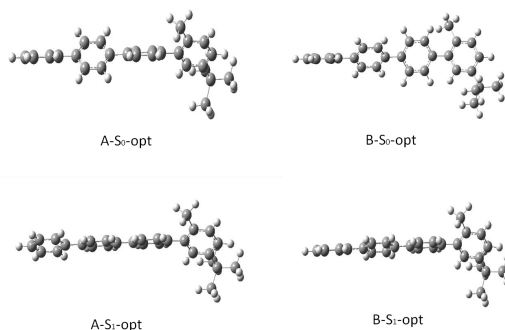


Figure 2: Geometries of DMQ and its conformers. A- S_0 -opt and B- S_0 -opt are the conformers of DMQ at S_0 . A- S_1 -opt and B- S_1 -opt are the conformers of DMQ at S_1 .

Steady-state results

The steady-state absorption spectra and fluorescence spectra of DMQ in ethanol at 293K are shown in **Figure 3**. The experimental results show an absorption peak at approximately 288 nm and three fluorescence peaks at approximately 345 nm, 360 nm, and 380 nm. The absorption spectra and fluorescence spectra of some chromophores are dependent on temperature. [32] Herein, the temperature dependence of the maximum absorption and fluorescence intensity of DMQ in ethanol at varying temperatures from 283 K to 343 K are shown in **Figure 4**. The more details of the change of absorption spectra and fluorescence spectra of DMQ in ethanol are shown in **Figure S1** (Supporting Information).

It is observed that the maximum absorption intensity decreased as temperature increased. And a small blueshift was observed as temperature increased. The decreased absorption intensity may be caused by the decreased of molar extinction coefficient with increased temperature. And the blueshift of absorption spectra may be caused by the increasing population on the blue area of ground-state. Similar to absorption spectra, the fluorescence intensity decreased as temperature increased and a slight blueshift was observed. According to **Figure 4**, at low temperature rang, the fluorescence and absorption intensity decreased at nearly the same rate. As a result, the decreased fluorescence intensity of DMQ is major due to the decreased absorption intensities. As temperature increased at higher temperature range, the decreased rate of fluorescence intensity is larger than that of absorption intensity, which may be caused by the enhancement of collisional effect and rotational relaxation.

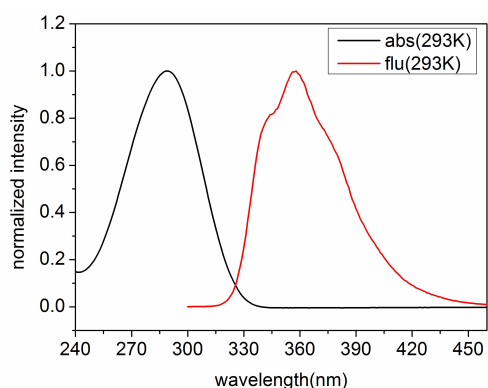


Figure 3: Absorption spectra and fluorescence spectra at 293K obtained by experiment in ethanol at 0.1 mM DMQ.

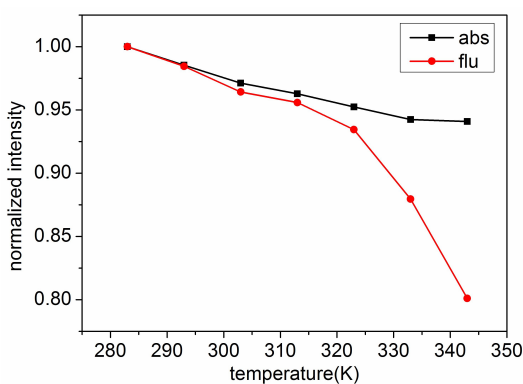


Figure 4: Temperature dependence of the maximum absorption and fluorescence intensity in ethanol at temperature range from 283K to 343K.

The temperature dependences of DMQ fluorescence lifetime in ethanol are shown in **Figure 5**. It is noted that the fluorescence lifetime of DMQ increased but fluorescence

intensity decreased as temperature increased. In general, the fluorescence lifetime of fluorophore should be decreased as temperature increased, similar to that of fluorescence intensity. [11] However, the fluorescence lifetime may vary because of other temperature-dependent processes.[12-17,33] It is well known that fluorescence lifetime can be expressed as $\tau = 1/(K_F + K_{non})$. Where K_F is the intrinsic emissive rate constant, and K_{non} is the non-radiative rate constant. For K_F , Strickler et al. reported that the decreased absorption extinction coefficient will lower the intrinsic lifetime (K_F). [33] On the other hand, with increased temperature; the viscosity of solvent decreased and may obtain larger K_{non} for the larger collisional quenching and rotational relaxation. However, the $K_F + K_{non}$ may be decreased as temperature increased because of the larger changes of K_F . As a result, DMQ will show longer lifetime at higher temperature.

From the steady-state absorption spectra and fluorescence spectra, the relative quantum yield may be obtained. Herein, the quantum yield Φ of DMQ at 283 K was selected as the standard. The temperature dependences of DMQ relative quantum yield in ethanol are shown in **Figure 6**. As temperature increased, the quantum yield increased slowly at low temperature and decreased quickly at high temperature, which reached a maximum at approximately 303 K. After the maximum point, the quantum yield decreased quickly as temperature increased.

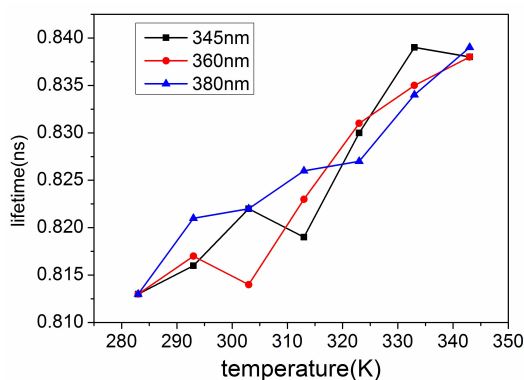


Figure 5: Temperature dependence of DMQ fluorescence lifetime in ethanol at emission wavelengths of 345, 360, and 380 nm at temperature range from 283K to 343K.

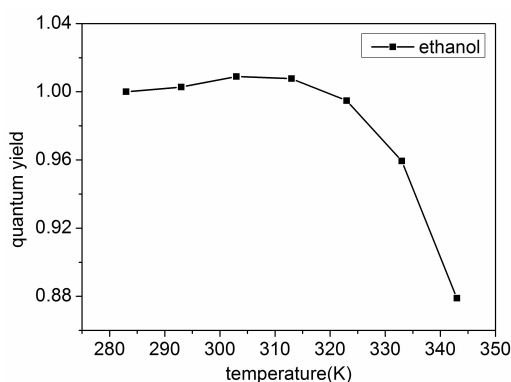


Figure 6: Temperature dependence of DMQ relative quantum yield in ethanol at temperature range from 283K to 343K. The quantum yield at 283K °C was selected as the standard.

Both K_F and K_{non} control the quantum yield, $\Phi = K_F/(K_F + K_{non})$. As discussed before, K_F decreased with increased temperature while K_{non} increased. Then, the quantum yield of DMQ should be decreased with increased temperature. However, experimental results show increased quantum yield at initial low temperature range (**Figure 6**). These unusual results can hardly be interpreted by two-emission-state mode. In order to understand the results,

femtosecond transient absorption spectra of DMQ were studied.

Transient absorption spectra

The femtosecond transient absorption spectra of DMQ in ethanol are shown in **Figure 7**. **Figure 7(a)** shows the femtosecond transient absorption spectra of DMQ in ethanol after pumping at 285 nm at decay time 0.5 ps, 1.0 ps and 2.0 ps. It is obtained that the signal intensity at 550 and 715 nm decreased as time decay (see the inserts in **Figure 7a**), whereas the signal intensity at around 620 nm increased. **Figure 7(b)** shows the transient absorption temporal profiles at 550, 620, and 715 nm. The 550 nm absorption signal decreased at 1.20 ps lifetime, whereas the 715 nm absorption signal decreased at 5.21 ps lifetime. The absorption signal at 620 nm increased at 0.66 and 5.90 ps lifetimes. These two increasing lifetimes of 620 nm correspond to the decreasing lifetime of 550 and 715 nm within the experimental deviations.

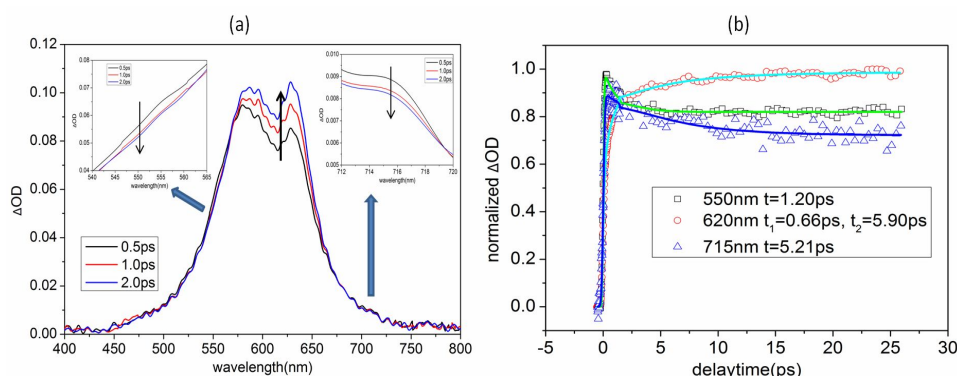


Figure 7: (a) Transient absorption spectra at decay time 0.5 ps, 1.0 ps and 2.0 ps of DMQ in ethanol. (b) Typical transient absorption temporal profiles of DMQ in ethanol after pumping at 285 nm and probing at 550, 620, and 715 nm. The solid lines denote the fitted curves, and the fitted lifetimes of them were noted.

Figure 2 show that the structures of DMQ have some torsion from the Franck-Condon states (S_1 -FC) to the optimized S_1 states (S_1 -opt). It is assume that the absorption signals at 550 and 715 nm are the absorption of the states which near the Franck-Condon states, called A- S_1 -FC (conformer A) and B- S_1 -FC (conformer B), respectively (**Figure 8**). The decreasing lifetimes 1.20 and 5.21 ps are then contributed by the internal conversion from A- S_1 -FC and B- S_1 -FC to S_1 -opt state, respectively. Obviously, this internal conversion accompanied with the molecular rotational dynamics. The decreasing lifetime of B- S_1 -FC is longer than that of A- S_1 -FC because the torsion angle from B- S_1 -FC to S_1 -opt is larger than the torsion angle from A- S_1 -FC to S_1 -opt, as discussed previously. From **Table 1**, the structure of A- S_1 -opt and

B-S₁-opt is similar, and the energies of these two structures are almost the same. So the states A-S₁-opt and B-S₁-opt can be treated as one state named S₁-opt. Then the absorption signal at 620 is assigned to the absorption S₁-opt.

Figure 8 shows the scheme of the excited-state decay dynamics of DMQ. A three-state-model was established here, A-S₁-FC, B-S₁-FC and S₁-opt control the fluorescence quantum yield of DMQ. It is assume that A(B)-S₁-FC states are emissive states. Equilibrium between S₁-FC and S₁-opt will be established after excited, for the signal at 550 nm and 715 nm does not go to zero. The fluorescence spectra of DMQ show that the fluorescence intensity at blue side increased with increased temperature. This may be contributed by the emission from high energy levels. It is well known that the populations at high energy levels will be increased with increased temperature. So that, the fluorescence come from S₁-FC state increased and then the fluorescence quantum yield increased at low temperature range. However, at higher temperature, the collisional and rotational effects may be the major effects. The collisional and rotational effects enhanced quickly at higher temperature rang (**Figure 4**), which quenched the fluorescence. Hence, the quantum yield decreased quickly at higher temperature.

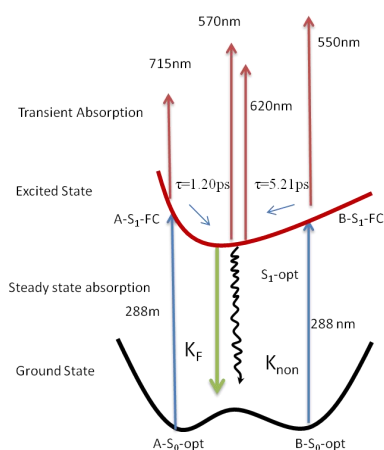


Figure 8: Fluorescence decay path and transient absorption process of DMQ.

Conclusion

The temperature studies showed the fluorescence lifetime of DMQ increased with increased temperature, whereas quantum yield increased slowly at low temperature range and decreased quickly at higher temperature range. As a result, a three-emission-state mode (A-S₁-FC, B-S₁-FC and S₁-opt) was established to explain the excited-state dynamics of DMQ. We conclude that the increase in fluorescence lifetime as temperature increased may be

mainly caused by the decreased absorption extinction coefficient. The quantum yield increased slowly initially is due that the population at high energy levels increased with increased temperature, and the rotational and collisional effects are not enough to quench the increased fluorescence from high energy levels. However, rotational and collisional effects are major when temperature increased sequentially, so the quantum yield decreased quickly at higher temperature range. Nevertheless, more theoretical and experimental works deserve further study to understand the temperature effect on fluorophores.

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