

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.

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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.

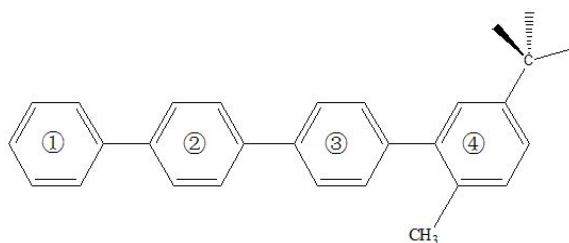


Figure 1: Structure of DMQ, with 1-4 as labels of the four benzene plane.

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