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Laser-induced temperature dependent triplet state lifetime of rubreneperoxide

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Abstract

A number of photophysical properties of three different types of rubreneperoxides have been measured experimentally by flash spectroscopy technique, including the two-photon absorption, fluorescence, delayed fluorescence and temperature dependent triplet–triplet absorption spectra. Excited singlet and triplet state lifetimes are temperature dependent. Lowest triplet state lifetimes were measured from 77 K to 50 °C. Experimental observations showed that as we decreased the temperature of rubreneperoxides, most of the molecules migrate to the lowest vibrational and rotational energy levels of the ground electronic state. Similar migration is also observed for the lowest triplet state. Therefore at 77 K, we can get the clean absorption an emission spectra and decay curves for the lowest triplet state. At 50 °C, due to the P- and/or E-type of delayed fluorescences, decay of T_1 state, in other words disappearance of the T_1 state is becoming faster than at low temperature (below room temperature).

Keywords: Rubrene; Rubreneperoxide; T–T absorption; T–T decay; Fused silica; Sensitized fluorescence

1. Introduction

The bright red hydrocarbon rubrene (hereafter R), (5,6,11,12 – tetraphenyltetracene), form three different oxides when irradiated by UV-light in the presence of molecular oxygen in solution. The colorless substance rubreneperoxides, (hereafter RO_2), obtained in this way is stable, contains no active hydrogen and hydroxyl absorption in the IR. Rubrene is widely used as singlet oxygen substrate to measure quantum yields of singlet oxygen production as well as the effectiveness of singlet oxygen quenchers. This substrate reacts cleanly to form photoperoxides according to the following reaction scheme. Fig. 1 shows the absorption and emission spectra of rubrene in solution.

$$^1R + h\upsilon \rightarrow {}^1R^*$$

$$^1R + O_2(^3\Sigma_g^-) \rightarrow {}^3R^* + O_2(^1\Delta_g)$$

$$^3R^* + O_2(^3\Sigma_g^-) \rightarrow {}^1R + O_2(^1\Delta_g)$$

$$^1R + O_2(^1\Delta_g) \rightarrow RO_2(\text{stable})$$

Or direct photo-oxygenation of rubrene, two rubrene molecules have to take part in the reaction sequence which leads to the stable endoperoxide.

- Reaction path (a):
  $R + O_2 \rightarrow (RO_2)$ unstable adduct formed in the dark. $R^* + (RO_2) \rightarrow RO_2$ (stable) + R
- Reaction path (b):
  $R^* + O_2 \rightarrow R + O_2^*$, electronic energy transfer to oxygen forming excited oxygen. $R + O_2^* \rightarrow RO_2$(stable)
- Reaction path (c):
  $R^* + R \rightarrow (R)_2^*$, formation of an activated double molecule (Excimer formation) $(R)_2^* + O_2 \rightarrow RO_2$(stable) + R

Since triplet ground-state oxygen does not seem to be produce cyclo-addition reactions, the production of endoperoxides may establish the presence of singlet oxygen in an oxidizing system.

The bright red hydrocarbon rubrene, (in C_{2V} symmetry), forms three different oxides when irradiated in the presence of molecular oxygen in solution. The three oxides of rubrene have similar absorption spectra. The colorless substance obtained in this way is very stable to have the molecular structures I, II and III

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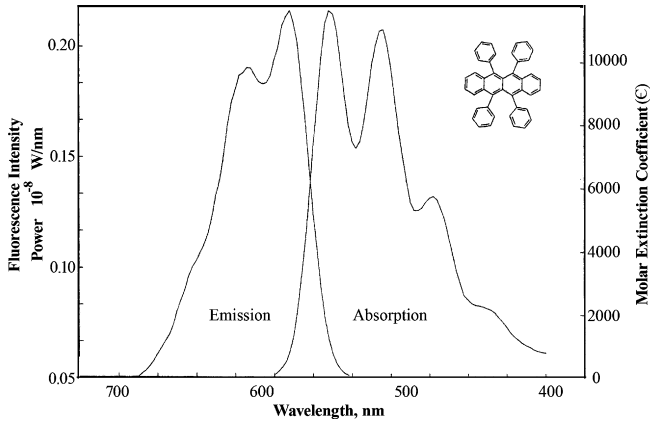

Fig. 1. The one-photon absorption and corrected prompt fluorescence spectra of rubrene in cyclohexane at room temperature (original spectrum is taken by the permission of F. Bayrakçeken).

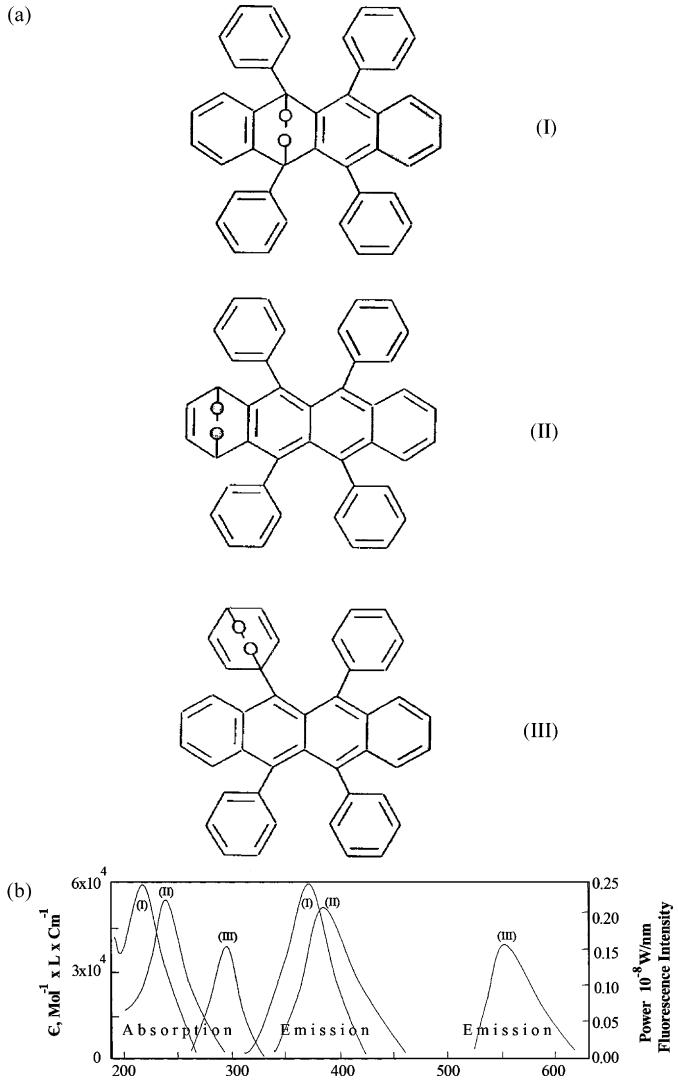

Fig. 2. (a) The obtained stable molecular structures of rubreneperoxides. (b) The one-photon absorption and corrected prompt fluorescence spectra of rubreneperoxides I, II and III structures in cyclohexane at room temperature.

as indicated in Fig. 2(a) and (b) shows the one-photon absorption and corrected prompt fluorescence spectra of rubreneperoxides I, II and III structures in cyclohexane at room temperature. It is stable to heat, because contains no active hydrogen and no hydroxyl absorption in the IR. It is also postulated that the formation of an unstable electronically excited rubrene–oxygen complex which should either dissociate into its components or be stabilized by collision with another rubrene molecule. The work reported here was undertaken with the aim of determining the values of spectroscopic parameters which are of significance to the photochemistry of the excited singlet and triplet states and to manufacture different optical sensors at different frequencies. For many organic compounds the pattern of vibrational levels is more complex and all the transitions to the various levels of the first excited state appear as one broad absorption band. The optical and electrical properties of peroxides may be chanced due to photobleaching and photoconversion of pre-existing point defects or to photogeneration of new ones. Moreover, by using ultraviolet irradiation, it has been recently shown that gratings can be written on optical fibers.

Isolated rubrene and rubreneperoxide molecules have been considered theoretically by performing molecular-mechanics and AMI type semi-emprical molecular-orbital (MO), self-consistent field (SCF) calculations within the Unrestricted Hartree–Fock (UHF) formulation. The geometry of the molecules considered has been optimized by molecular-mechanics method using MM + force field, then single point electronic energy calculations have been performed by AMI method (Auston Model 1). Geometry optimization has been carried out by using a conjugate gradient method, Polak–Ribiere algorithm. All the calculations have been performed by using the HyperChem-5.1 package program [1–21].

2. Experimental

The rubrene was Aldrich reagent grade and used as received, at a concentration of 2.65×10^{-5} M in different solvents. All other chemicals used were of reagent grade. Absorption spectra were recorded using a Cary 219 spectrophotometer. An SLM-8000-S fluorimeter was used to obtain fluorescence and excitation spectra. Fluorescence lifetimes were determined with a PRA single photon counting nanosecond fluorescence spectrometer interfaced to a Terak 8510 graphic system for data analysis, storage and display.

The triplet related transient phenomena were studied in a laser flash photolysis setup consisting of the following: a Molectron UV-400 nitrogen laser system at 337.1 nm, Nd: YAG laser at 266, 532 and 1064 nm, and Excimer laser at 248 nm, for excitation. A kinetic absorption spectrometer with nanosecond response (pulsed 500-W, xenon lamp, B&L, UV-visible high intensity monochromator, and RCA 4840 photomultiplier tube with output signal terminated into 93 Ω), a Tektronix 7912 digitizer and LSI-11 micro-processor unit that controlled the experiments and processed the data at the initial stage. The data from LSI-11 were finally transferred to a time shared PDP 11/55 computer system for storage and further treatment. The flash photolysis experiments were carried out on oxygen free, (degassed in