



# Excited-state energy levels and photophysics of a short polyene 2-(4-phenyl-1,3-butadien-1-yl)thiophene



Takao Itoh

Graduate School of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan

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## ABSTRACT

Emission, excitation and absorption spectra of a new and short polyene, 2-(4-phenyl-1,3-butadien-1-yl)thiophene (PBT), have been measured under different conditions by varying temperature and solvent and in the vapor phase, along with those of 2-(2-phenylethenyl)-thiophene (PET). The presence of a forbidden excited singlet state, located at energies slightly below the strongly absorbing state, is indicated for PBT, although the forbidden state was not identified for PET. The emission of PBT consists of fluorescence from the allowed  $S_2$  and forbidden  $S_1$  states in low polarizable solvents, while it consists of fluorescence mainly from forbidden  $S_1$  in the vapor phase and that from allowed  $S_1$  state in high polarizable solvents. Quantitative analysis of the temperature dependence of the  $S_1$  and  $S_2$  fluorescence spectra provides the  $S_1$  and  $S_2$  state energies and physical parameters that characterize the excited states of PBT.

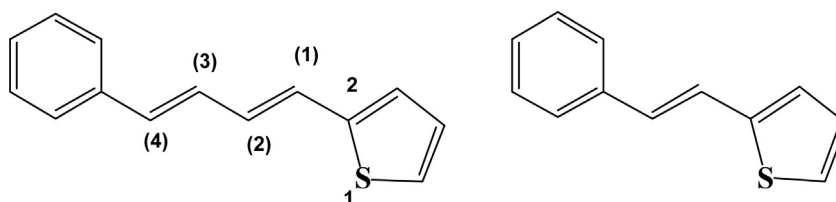
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## 1. Introduction

Polyene structure plays important roles in photosynthesis, visual pigments and other biological systems including vitamin A as well as in conducting polymers [1]. In particular, clarification of the excited-state electronic structures of short polyenes attracts much attention in conjunction with the electronic structure of diphenylbutadiene or unsubstituted butadiene. The  $S_1$  and  $S_2$  states are considered to be closely located to each other for shorter polyenes. Most of symmetrically substituted *all-s-trans* polyenes such as  $\beta$ -carotene belong to the  $C_{2h}$  point group. These  $C_{2h}$  polyenes exhibit an intense absorption band based on an allowed electronic transition,  $1^1A_g(S_0) \rightarrow 1^1B_u(\pi, \pi^*)$ , in the UV–vis region. The  $1^1B_u(\pi, \pi^*)$  state had been considered to be the  $S_1$  state for long time, but the existence of a forbidden excited singlet state,  $2^1A_g$ , located at energies below an allowed  $1^1B_u$  state, was pointed

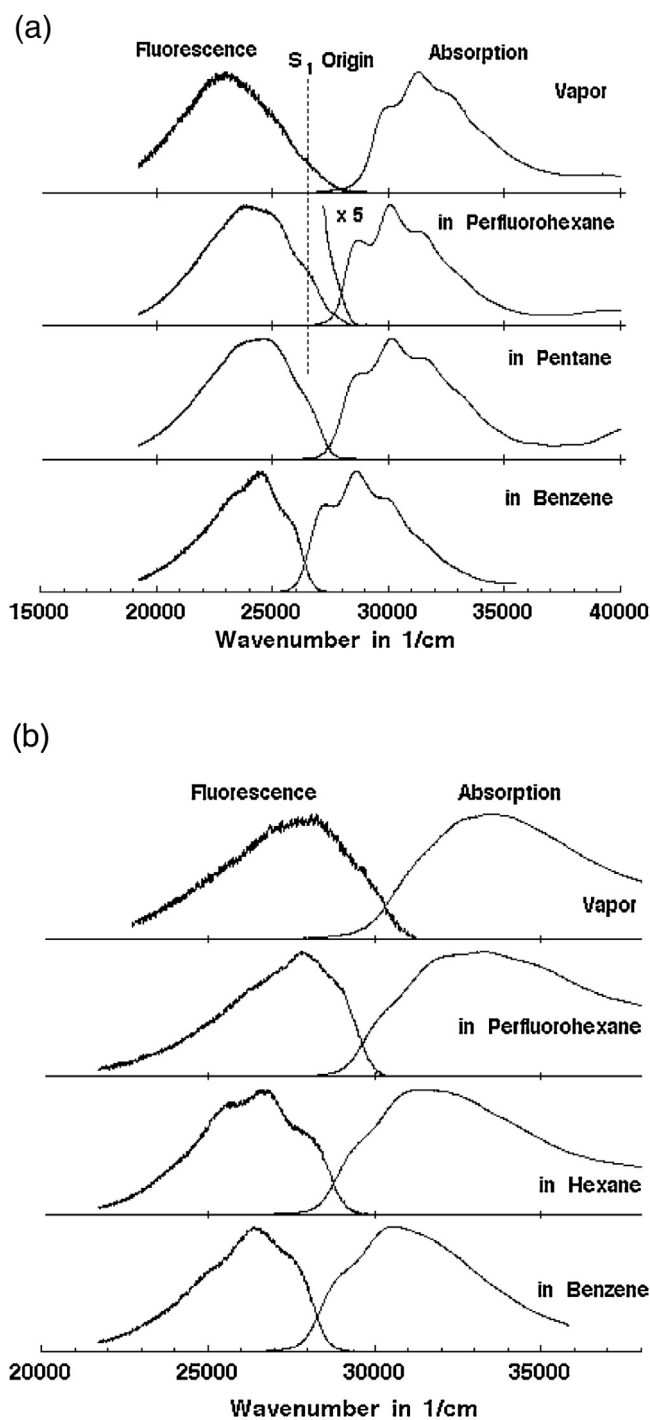
out in 1972, followed by theoretical interpretation of the  $2^1A_g$  state [2–4]. Since these findings, a number of studies have been carried out concerning the excited states of polyenes [5,6], although the presence of the forbidden  $S_1$  state of polyenes does not seem to be well known for most of chemists even at present. Thus, it is of necessity to accumulate the data showing the presence of the forbidden lowest singlet excited state of short polyenes other than the ones investigated heretofore. It is normally difficult to observe directly the transition to the forbidden  $S_1$  state in room temperature solution, because it is masked by strongly allowed absorption to the  $S_2$  state, which is located at energies slightly higher than the  $S_1$  state, and because it is dipole-forbidden. The forbidden  $S_1$  state of polyenes is considered to obtain its one-photon transition intensity mainly through the vibronic coupling with the allowed  $S_2$  state.

Molecular structures of PBT (left) and PET (right)

E-mail address: [titoh@hiroshima-u.ac.jp](mailto:titoh@hiroshima-u.ac.jp) (T. Itoh).

Since most of the all *trans*-polyenes with the polyene double bond number over 3 are considered to possess a characteristic forbidden  $S_1$  state, it must be of interest to investigate the electronic spectra of polyenes of various types. However, the number of commercially available polyene molecules is extremely limited. In the present study, a new short polyene, 2-(4-phenyl-1,3-butadien-1-yl) thiophene (hereafter abbreviated by PBT) has been synthesized and the spectroscopic properties were investigated under different conditions. A close relative, 2-(2-phenylethenyl)-

thiophene (PET), also has been synthesized and the spectroscopic properties were investigated under different conditions. Although the symmetries of PBT does not belong strictly to the  $C_{2h}$  point group, the electronic structures of the  $\pi \rightarrow \pi^*$  excited states are expected to be similar to those of the  $C_{2h}$  polyenes. The existence of a forbidden lowest singlet excited state located at energies slightly below a strongly absorbing state is indicated for PBT. It is shown also that the emission of PBT consists of dual fluorescence from the  $S_2$  and  $S_1$  states in low polarizable solvents, while it consists mostly



**Fig. 1.** (a) Absorption and corrected emission spectra of PBT in different solvents at room temperature and in the vapor phase. Vapor-phase emission spectrum was measured at 95 °C in the presence of 760 Torr  $N_2$ . The emission spectra were obtained by excitation into the  $S_2$  state (around 300–330 nm). All the spectra are normalized to a common magnitude. Broken line indicates the location of the  $S_1$  state. (b) Absorption and corrected emission spectra of PET in different solvents at room temperature and in the vapor phase. Vapor-phase emission spectrum was measured at 80 °C in the presence of 760 Torr  $N_2$ . The emission spectra were obtained by excitation into the  $S_2$  state (around 310 nm). All the spectra are normalized to a common magnitude.

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