Fluorescent Aggregates of 1-(*p*-Butyloxyphenyl)-4-(*p*-cyanophenyl)Buta-1*E*,3*E*-Diene: Temperature Sensing and Photoimaging Applications

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The use of fluorescent solid films of a 1-(*p*-butyloxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*, 3*E*-diene as an efficient temperature sensor is described. The fluorescence changes in these films are proposed to occur due to a reversible temperature-dependent variation in its monomer-aggregate ratio. Photoisomerization of the butadiene chromophore in solid films was observed to occur only at elevated temperatures ($>120°C$), making the material also useful for reversible photochemical generation of fluorescence patterns with nondestructive readout properties.

INTRODUCTION

Development of fluorescent sensors for various analytes such as ions, biomolecules, and gases has been an active area of research [1–3]. More recently there has been a growing interest in the development of molecular sensors for monitoring changes in environmental parameters such as temperature [4–6]. Fluorescence thermometry provides a noncontact sensing strategy relying on the temperature dependence of fluorescence of materials, and this has several advantages over conventional contact methods [7,8]. With very few exceptions, however [9–12], most studies on fluorescence-based temperature sensors have been carried out in the solution phase [7,13–15]. For several practical applications, immobilization of the temperature-sensitive fluorescent materials in solid matrices is required, especially with respect to mapping temperatures on two-dimensional surfaces of varying contours. Immobilization of such probes onto solid surfaces frequently leads to quenching of fluorescence due to aggregation [16]. Contrary to this understanding, however, there are several recent examples where organic materials become strongly fluorescent upon forming aggregates in solid films [17–22]. The propensity of molecular systems to form such fluorescent aggregates has been attracting increasing attention since their unique optical properties make them useful in a wide range of applications such as in organic light emitting diodes [23–24], optical imaging and laser development [25–29]. Cao *et al.* have recently reported on the use of such materials for sensing organic vapors [30]. Aggregation is generally a thermodynamically controlled process, although in certain cases the process can be kinetically controlled. In view of this the solid state fluorescence of many of these materials could potentially be sensitive to temperature. However their use as temperature sensors has hitherto not been explored. Here we report on highly fluorescent aggregates of 1-(*p*-butyloxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-diene (**BC**, Fig. 1) whose formation in the solid state is remarkably sensitive to temperature making it a promising temperature sensing material. Additionally we also report on the ability of this material to exhibit bistable photoswitching between states possessing different fluorescence, making it a useful optical memory recording medium.

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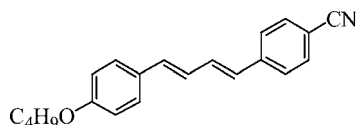[2] To whom correspondence should be addressed. E-mail: sdaas@rediffmail.com

Fig. 1. 1-(butyloxyphenyl)-4-(cyanophenyl)buta-1*E*,3*E*-diene (**BC**).

EXPERIMENTAL SECTION

The synthesis of the butadiene derivative has been reported earlier [31]. Thin solid film of the butadiene derivative was prepared by melting it between two glass slides and allowing it to cool. Solid state emission spectra were recorded using a front face emission scan mode on a SPEX Fluorolog F112X spectrometer. Absorption spectrum was recorded on a Shimadzu UV-Vis-NIR 3101 PC spectrophotometer and reflectance spectrum was recorded by attaching a Shimadzu integrating sphere assembly to the spectrophotometer. BaSO$_4$ was used as the 100% reflectance standard. Temperature variation of the sample for the solid state fluorescence switching experiment was carried out using a Linkam THMS 600 hot stage connected to a Linkam TP92 temperature programmer. Fluorescent images were recorded using 360 nm monochromated light from the 500 W Xenon lamp source of SPEX Fluorolog F112X spectrometer. The sample was maintained at 130°C using Linkam THMS 600 heating and freezing stage connected to a Linkam TP92 temperature programmer. Laser irradiation was carried out using the fourth harmonic (266 nm, 15 mJ/pulse, pulse width 10 ns) of a Quanta Ray GCR-12 Nd:YAG laser.

RESULTS AND DISCUSSION

The solution state absorption and emission spectra of **BC** along with its solid state diffuse reflectance absorp-

tion and emission spectra are shown in Fig. 2. In toluene, **BC** possesses fairly sharp absorption and emission spectra with the absorption maximum centered on 365 nm and the fluorescence maximum centered on 435 nm. In a more polar solvent such as acetonitrile the fluorescence maximum shifts to 480 nm. The absorption spectrum of the opaque solid sample was obtained by recording its diffuse reflectance absorption spectrum. Its absorption and emission spectra in the solid state are substantially broadened indicating the presence of aggregated species. The diffuse reflectance absorption spectrum of the solid film of **BC** possesses two maxima centered at 370 and 450 nm, respectively and its solid state emission spectrum is considerably red-shifted with maxima at 464 and 495 nm and a prominent shoulder around 520 nm. We have recently shown that the broadening of the fluorescence spectrum and the formation of a new red-shifted band in the absorption spectrum of solid films of 1-(*p*-alkoxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-dienes, can be attributed to the formation of aggregates [32].

The solid state fluorescence intensity of **BC** was observed to be highly sensitive to temperature. With increase in temperature, the intensity of fluorescence of a solid film of BC decreased significantly (Fig. 3), and this was accompanied by a gradual blue-shift and narrowing of the fluorescence spectrum, with the peak at 495 nm and the shoulder around 520 nm becoming less prominent at higher temperatures. Figure 3 (inset) depicts the change in fluorescence intensity at 520 nm with increase in temperature.

The change in fluorescence of BC caused by heating was fully reversed on cooling. The change in fluorescence intensity at 520 nm, upon repeated heating and cooling cycles over various temperature ranges is depicted in Fig. 4. The temperature-induced fall in the fluorescence intensity was observed to be proportional to the temperature attained, and the fluorescence
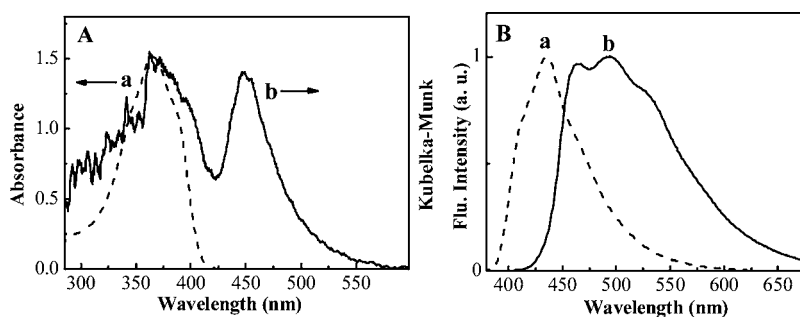

Fig. 2. Absorption and fluorescence spectra of BC; (A) (a) absorption spectrum in toluene and (b) diffuse reflectance absorption spectrum of solid film, (B) (a) Fluorescence spectra in toluene and (b) solid film.
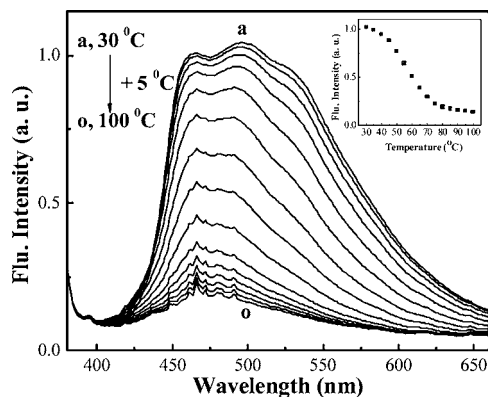
Fig. 3. Solid state fluorescence spectra of **BC** at various temperatures; inset: change in fluorescence intensity at 520 nm as a function of temperature. Excitation wavelength: 360 nm.

switching between various temperature ranges was highly reproducible.

As discussed above the broad emission of solid films of **BC** at lower temperatures arises predominantly from aggregates [32]. The blue-shift in the emission band, accompanied by a narrowing and loss of intensity of the band may be attributed to a reduced ground-state interaction of the molecules leading to monomer-like fluorescence and enhancement in the nonradiative decay due to increased vibrational and rotational freedom of the molecules at higher temperatures. **BC** exhibited efficient reversible fluorescence switching over a useful temperature range of 30–100°C. Although butadiene derivatives are known to undergo photoisomerization, continuous exposure of a solid film of **BC** to 360 nm excitation light
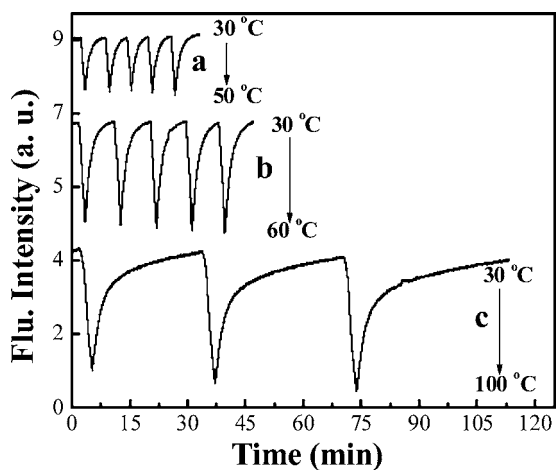
used to monitor the temperature variations (Fig. 4), did not lead to any permanent change in its fluorescence, indicating that the material was photochemically stable under these conditions. This can be attributed to the known viscosity dependence of photoisomerization of polyenes, where *trans* to *cis* photoisomerization is prevented in the solid state but the reverse *cis* to *trans* photoisomerization remains feasible [33–35]. At temperatures close to and above the melting point of **BC** (141.5°C) however, photoisomerization of the *EE* isomer was observed while monitoring the fluorescence changes as a function of temperature. This resulted in a loss of fluorescence during the measurement cycle (Fig. 5).

The occurrence of photoisomerization close to the melting point could be advantageously utilized for photoinduced recording of fluorescent images on thin films of BC. Photolysis of a solid film of BC maintained at 130°C with 360 nm light, led to a hypsochromic shift in its solid state fluorescence. The fluorescence of the irradiated regions changed from green to blue (Figs. 6 and 7). The fluorescence change observed in the photolyzed regions of these films could be attributed to the formation of photoisomers (*EZ* and *ZE*) of **BC** [31]. Since the isolation the photoisomers of **BC** by HPLC proved to be difficult, conformation of the above was obtained by observation of the blue solid state fluorescence of the photoisomers of 1-(*p*-methoxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-diene isolated using HPLC [36]. It is of interest to note that the photoisomers are nonfluorescent in solution.

A general drawback associated with most reported photochromic imaging systems is that both "write" and "read" processes use light of nearly same wavelengths [37,38]. Due to this, recorded images can be

Fig. 4. Fluorescence switching between (a) 30 and 50°C, (b) 30 and 60°C, and (c) 30 and 100°C; emission monitored at 520 nm; heating rate 20°C/min and cooling rate 5°C/min. Excitation wavelength: 360 nm.
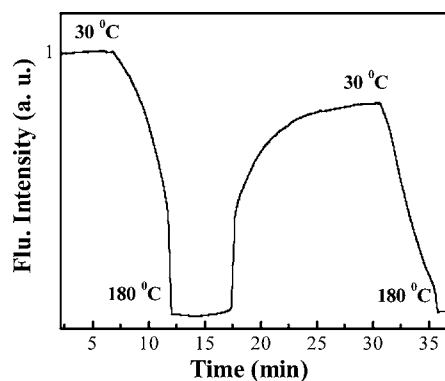

Fig. 5. Fluorescence switching monitored between 30 and 180°C. At high temperatures >120°C, full recovery of fluorescence is not observed due to photoisomerization caused by the excitation light at higher temperatures. Excitation wavelength: 360 nm.
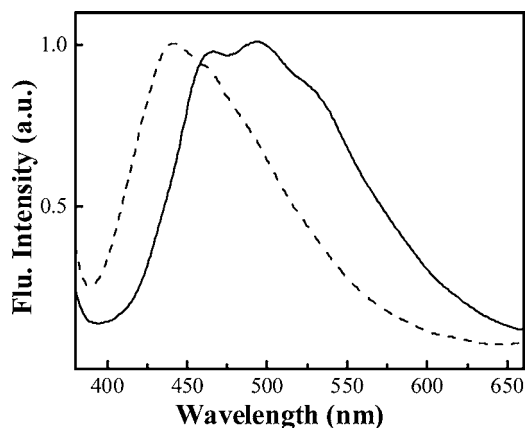
Fig. 6. Solid state fluorescence at room temperature from the imaged (—) and unimaged (- - -) portions of the photoimage created using **BC**.

blurred or destroyed by photoreactions initiated during the "read" process. Several strategies have been adopted to try and overcome this problem [37–42]. In the present system, since the photochemical transformation occurs only at elevated temperatures, and repeated reading of the images using light at ambient temperatures does not result in erasure or blurring of the recorded images. In the solid state at ambient temperatures the *Z*-photoisomers of 1-(*p*-alkoxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-dienes could however be converted back to their *EE* isomer upon photolysis using 266 nm laser [31]. This stereospecific photoisomerization property in the solid state could be favorably utilized for erasure of the recorded images on solid films of **BC**.

Fig. 7. Photoimage recorded on a thin film of **BC** using 360 nm light and an appropriate mask. The green fluorescent portion (*EE* form) is unphotolyzed and the blue fluorescent portions (*EZ, ZE* forms) were formed upon photolysis.

CONCLUSIONS

In conclusion, we report on the high sensitivity of solid state fluorescence of 1-(*p*-butyloxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-diene that makes it useful for temperature sensing applications. It is envisaged that encapsulation of this material using suitable polymers will enable it to detect temperature changes in the solution phase also. In addition, the ability to record fluorescent images at high temperatures with nondestructive readout properties at ambient temperatures in a reversible manner makes it a useful photoimaging material.

ACKNOWLEDGMENTS

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