

## Emission Control of a Pyrene-thioindigo Compound

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Two distinct fluorescence modes of a thioindigo compound substituted with two pyrene groups on the 7 and 7' positions were controlled by geometrical photoisomerization of the thioindigo skeleton.

Recently photochromic materials have been investigated for molecular-size optical memory and optical switching.<sup>1</sup> There are a number of investigations of photochromic memory applied to the absorption changes of photochromic materials.<sup>2</sup> The absorption change memory has an inherent problem in that the memory would be destroyed by a 'reading light' that causes reverse photoisomerization. Herein we study a pyrene-thioindigo compound that in either the *trans* or *cis* conformation could be read using not only absorption change but also fluorescence change.

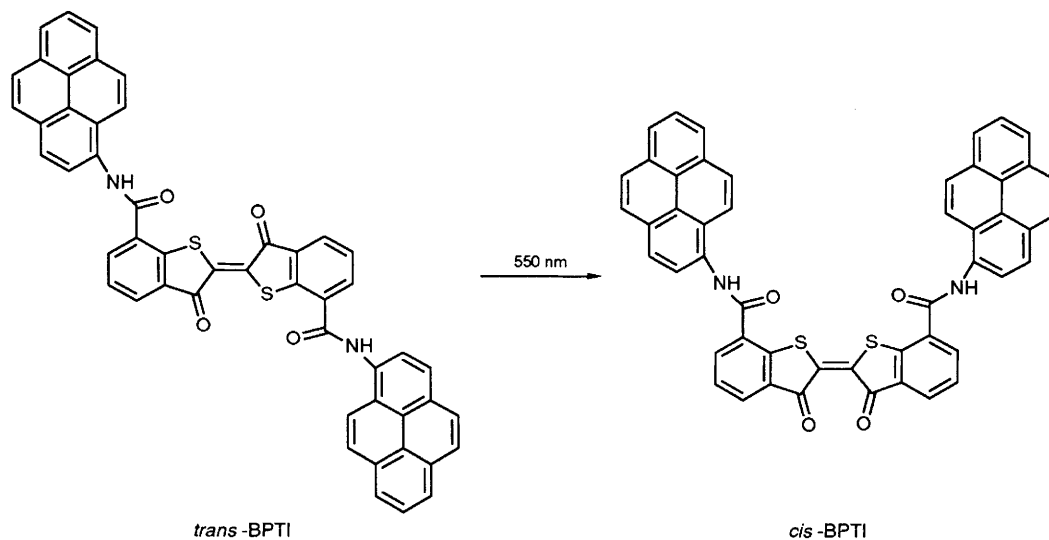
A thioindigo compound, shows typical photochromism resulting from geometrical photoisomerization between its *trans* and *cis* forms.<sup>3</sup> On the other hand, pyrene is a typical fluorescence chromophore. It is known that pyrene has two distinct emission modes, a monomeric mode and an excimeric mode by association. Formation of the intramolecular excimer is controlled by the distance between two pyrene groups. An investigation of series of bis(1-pyrenyl)alkenes,  $\text{Pyn}(\text{CH}_2)_n\text{Pyn}$ , showed that the formation of an intramolecular excimer was controlled by the alkyl chain length.<sup>4</sup> The strongest emission from the intramolecular excimer was observed at  $n = 3$  according to the Hirayama rule.<sup>5</sup>

A pyrene-thioindigo compound substituted with two pyrene groups at the 7 and 7' position, 7,7'-bis(1-pyrenylaminocarboxy)thioindigo (BPTI), was synthesized according to a procedure similar to that which Irie and Kato used to synthesize 7,7'-bis(alkoxycarbonyl)thioindigo.<sup>6</sup> Scheme 2 shows the synthetic pathway. This compound was obtained as a red-violet powder after purification by column chromatography.

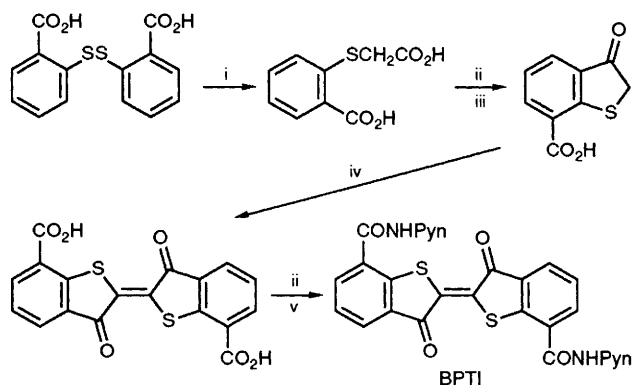
Fig. 1, lines A and B, show the photochromic absorption change of BPTI in  $\text{CHCl}_3$  ( $4.0 \times 10^{-6}$  mol  $\text{dm}^{-3}$ ) at room temperature. *trans*-Thioindigo, with an absorption maximum at 542 nm, is converted to *cis*-thioindigo, with an absorption maximum at 481 nm, upon irradiation with light at a wavelength of 550 nm. A similar spectral change was observed for BPTI. Synthetic BPTI showed an absorption maximum at 540 nm due to the *trans* form, Fig. 1, line A. This absorption maximum was decreased under irradiation with light at

550 nm, and the new absorption maximum, at 490 nm, was increased while keeping the isosbestic point at 510 nm (Fig. 1, line B). The spectrum change was saturated by irradiation with a light of 550 nm for 15 min. This spectrum change implied that the converted compound was *cis*-BPTI. The spectrum was then converted back by irradiation at 480 nm for 20 min whilst maintaining the isosbestic point.

Fig. 1, lines C and D, show the fluorescence spectra of BPTI followed by its photoisomerization at room temperature. It was measured in the same  $\text{CHCl}_3$  solution used for observing the photochromism; 340 nm light was used for excitation, because the pyrene unit has a large absorption at this wavelength but the thioindigo absorbs only slightly. Accordingly, the conformation of the thioindigo skeleton is expected to be retained after irradiation by the excitation light. Indeed, the absorption spectrum of BPTI was not changed after measuring the fluorescence spectra five times. *trans*-BPTI (before irradiation at 550 nm gave a fluorescence spectrum (line C) with emission bands at 380 and 410 nm. These emission bands were in a similar region to those of monomeric pyrene. The emission band at 590 nm was assigned to fluorescence from the *trans*-thioindigo skeleton of BPTI.<sup>7</sup> After irradiation at 550 nm for 15 min, a fluorescence spectrum change was observed (Fig. 1, line D). The monomeric emission bands of pyrene groups at 380 nm and 410 nm were strongly quenched and a new broad emission band at a longer wavelength of about 450 nm appeared. Two possible causes are considered as reasons for such a broad emission band. The first is the intramolecular excimer of the two pyrene groups. The other is an intramolecular heteromer of the pyrene group and the *cis*-thioindigo skeleton. If the pyrene group and the *cis*-thioindigo skeleton form an intramolecular heteromer on excitation, a mixture of them might show the presence of the intermolecular heteromer. A 2:1 mixture of 1-aminopyrene and thioindigo in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) did not give a quenching of the emission bands at 380 and 410 nm or show the appearance of new broad band after irradiation at 550 nm. Accordingly, this fluorescence spectrum change suggested that the new broad emission band at about 450 nm was



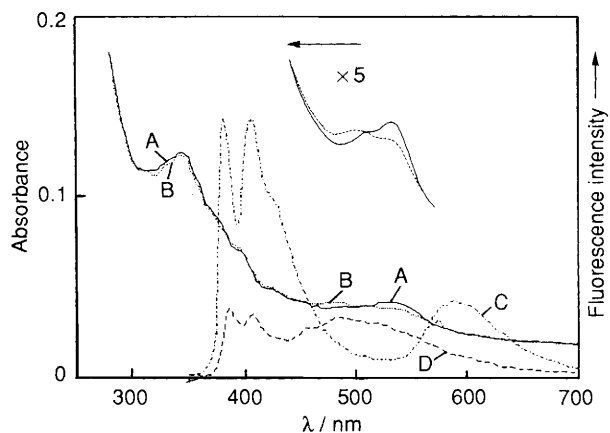
Scheme 1



**Scheme 2** Reagents and conditions: i,  $\text{ClCH}_2\text{CO}_2\text{H}$ ,  $\text{NaOH}$ ; ii,  $\text{SOCl}_2$ ; iii,  $\text{AlCl}_3$ , *o*-dichlorobenzene,  $50^\circ\text{C}$ ; iv,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{NaOH}$ ; and v, 1-aminopyrene, pyridine

assigned to an intramolecular pyrene-excimer emission in *cis*-BPTI. The emission band of *trans*-BPTI at 590 nm was also quenched after irradiation at 550 nm. This quenching showed that the thioindigo skeleton was isomerized from the *trans* form to the *cis* form, because it is known that *cis*-thioindigo does not show fluorescence.<sup>7</sup> Consequently, this result indicates that two pyrene groups of the *trans*-BPTI cannot interact. On the other hand, two pyrene groups of *cis*-BPTI when close enough can make an intramolecular excimer. The distance between the two pyrene groups was changed drastically by the *trans*-*cis* isomerization of the thioindigo skeleton.

By responding to each different wavelength of light, BPTI showed the photochromism of the thioindigo skeleton and the fluorescence of the pyrene groups. The emission modes of the pyrene groups, either monomeric or excimeric, were controlled by photoisomerization of the thioindigo skeleton. This unique function of BPTI may be exploited as follows. Firstly, the photochromic memory of BPTI can be read not only by the absorption change but also by the fluorescence change. Secondly, a wavelength change transducer using BPTI can select two emission modes for the signal output by controlling



**Fig. 1** UV/VIS and fluorescence spectra of BPTI: A, UV/VIS spectrum of *trans* form; B, UV/VIS spectrum of *cis* form; C, fluorescence spectrum of *trans* form; and D, fluorescence spectrum of *cis* form

the light used for the photoisomerization. This type of molecule can be expected to have application in optical logic computing.

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