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Unusual stability of thermally induced colored isomers of photochromic 3-aryl-3-(1-naphthyl)-3*H*-naphtho[2,1-*b*]pyrans in solid state

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ABSTRACT

Pure solid colorless powder of photochromic 3-aryl-3-(1-naphthyl)-3*H*-naphtho[2,1-*b*]pyrans were converted to their colored isomers in molten state. The solid colored isomers exhibit unusual stability at ambient temperature.

Developing materials having bistable forms that sense and respond to environmental stimuli and chemical signals on both microscopic and macroscopic levels has been a longstanding scientific pursuit.[1] This pursuit is brought about by the fact that molecules with stimuli-switchable characteristics are of considerable practical and fundamental interests, such as application in molecular switches, data storage media, logic gates, and so on.[2–9]

Typical bistable molecules are known as photochromic compounds, whose isomers with different absorption spectra exhibit a reversible change induced by light irradiation.[10,11] Of all potential applications of photochromic compounds, data storage is an important and attractive field.[12] The basic requirements for data storage are bistability and nondestructive detection.[13] For most photochromic naphthopyrans, the ring-opening and ring-closing interconversion is usually triggered by photoinduction (Scheme 1).[10] Several photochromic naphthopyrans compounds also exhibit thermochromic phenomenon such as a color change between two states of a molecule at varying temperatures.[11,14–16] However, naphthopyrans usually exhibit T-type photochromism, wherein fast fading after thermo irradiation is one of its intrinsic characteristics; the ring-open colored isomers transoid-*cis* (TC) and transoid-*trans* (TT) revert to their ring-closed form within minutes.[14–16] To address this problem, an efficient strategy has to do with the steric or substituent effect in a molecule to suppress isomerization.[17] To date, obtaining thermally induced colored isomers of naphthopyrans in pure solid powder state with good stability at ambient temperature, which would produce a new family of photochromes that could be of critical use in advanced applications, remains challenging.

Herein, we demonstrate a family of naphthopyrans with a 1-naphthyl group located at the 3-position (Scheme 2) that exhibits high optical density in solutions and force-induced cleavage of C—O bond characteristic, as shown in our previous work.[18,19] These naphthopyrans exhibit thermo-responsive behavior in pure solid powder state that could be converted to a colored state upon heating to their melting point. In contrast to the previous Letters,[14–16] the colored species of such naphthopyrans are hard to revert to their original colorless form in solid state at ambient temperature. Moreover, the color of the molten species can be determined by another substituent located in the 3-position of these naphthopyrans.

The thermal response of the pure solid naphthopyran powders was studied using an X4 melting point apparatus. When heated close to their melting points, the powders show a weak color change on their surface, which was then converted to an intense color when heated to their melting points. As presented in

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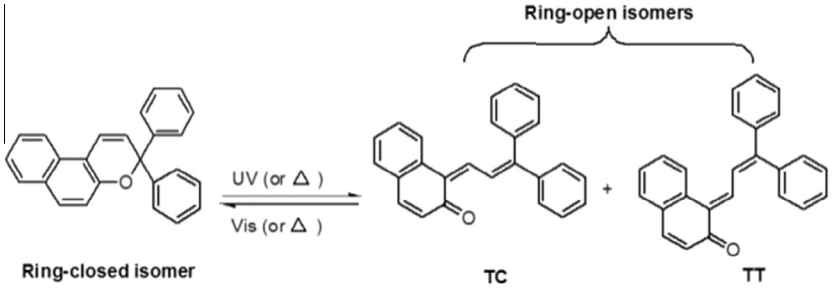
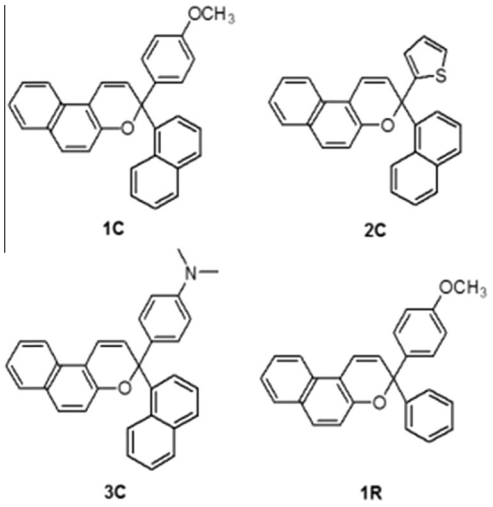
0040-4039/



Scheme 1. Photochromism or thermochromism of naphthopyran.



Scheme 2. Chemical structure of naphthopyrans 1C, 2C, 3C and 1R.

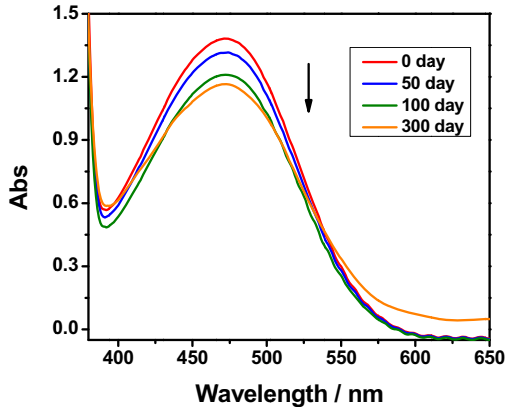


Figure 2. Solid absorption changes of T1O solid at ambient temperature.

Figure 1, the colorless powder of 1C is converted to an orange molten species T1O with λ_{max} at 472 nm upon heating to its melting point at 148–151 °C. To test the general nature of thermally induced chromism in naphthopyrans with a 1-naphthyl group located at the 3-position, powders of 2C and 3C were also employed. Both 2C and 3C showed similar thermally induced chromism to that of 1C. After heating 2C and 3C to their melting point at 130–133 °C and 198–201 °C, respectively, they were converted to different color species as bordeaux T2O and dark purple T3O with λ_{max} located at 474 and 569 nm, respectively, as shown in Figures S1 and S2. The XRD patterns of the thermally induced colored solid state of T1O, T2O, and T3O exhibit only a diffuse band, suggesting the amorphous nature of the solids (Fig. S3). The different melting points and molten colors of 1C, 2C, and 3C can be reasonably ascribed to the substituent effect of another substituent group located on the 3-position, namely, 4-methoxyphenyl (1C), thienyl (2C), and 4-dimethylaminophenyl (3C).

Unlike previous Letters stating that naphthopyrans undergo color-fading to revert to their original colorless state in a short period of time,[14–16] the present study found that decoloration was barely observed by the naked eyes for T1O, T2O, and T3O after their transfer into ambient temperature conditions for a long period of time. As presented in Figure 2, the colored T1O isomers exhibit an unexpected enhanced stability at ambient temperatures. In detail, the absorbance only decreases by approximately 4.7% for

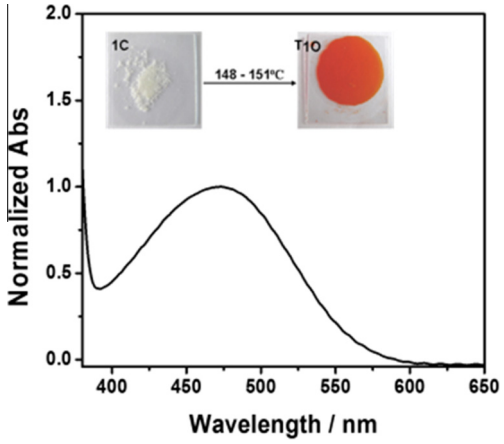


Figure 1. Solid state absorption spectra of T1O. Insert: image of thermally induced color changing of 1C to T1O.

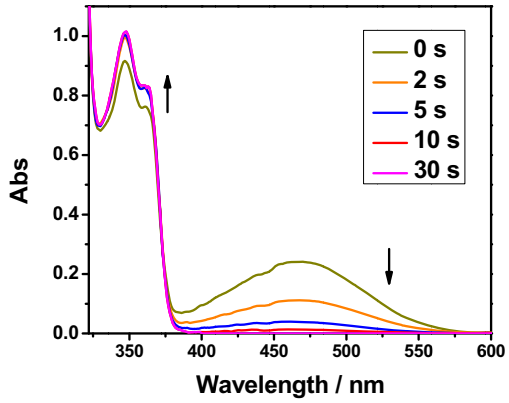


Figure 3. Absorption changes of T1O in dilute toluene solution (1×10^{-4} M) under visible light irradiation till colorless state.