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Design and Synthesis of an *o*-Hydroxyphenyl-Containing Spiropyran Thermochromic Colorant

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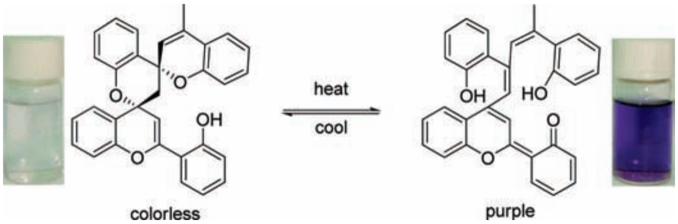
ABSTRACT



An *o*-hydroxyphenyl-containing spiropyran thermochromic colorant was designed and synthesized. The prepared compound is sensitive to temperature and has a reversible color change with temperature variation. X-ray diffraction analysis and variable-temperature NMR studies suggest that the thermochromism of the compound presumably involved a ring-opening C−O bond cleavage of the spiropyran moiety followed by an intramolecular hydrogen transfer.

Thermochromism refers to a reversible thermotransformation of a chemical species between two forms having different absorption spectra.[1] Compounds with thermochromic properties may have a wide range of applications in areas such as temperature-indicating devices, temperature-sensitive light filters, optical switching, imaging systems, etc. Various materials have been reported to exhibit thermochromism, which include organic compounds, inorganic compounds,[1b,2] polymers,[3] and sol−gels.[4] The most well-known organic thermochromic colorants are spiroheterocyclic compounds,[5] salicyl-Schiff bases,[6] and overcrowded ethylenes.[7] Previous studies have demonstrated that the mechanism responsible for organic thermochromism varies with the molecular structure. It may be due to an equilibrium between two molecular species, between two stereoisomers, or variation in crystal structures.[1d,8] For instance, the thermochromic mechanism of spiropyrans has been identified to involve a thermally sensitive equilibrium between the spiroheterocyclic form and the colored quasi-planar open merocyanine-like structure formed by the ring-opening C−O bond cleavage.

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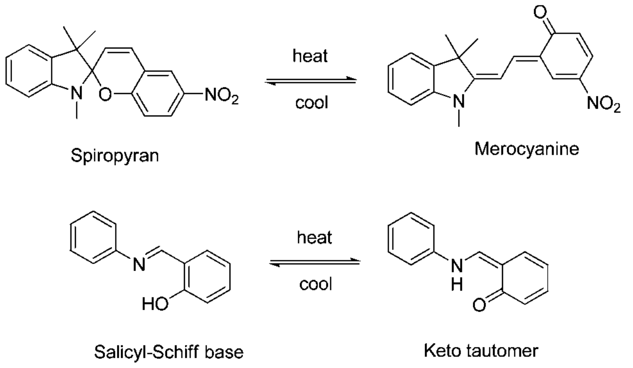
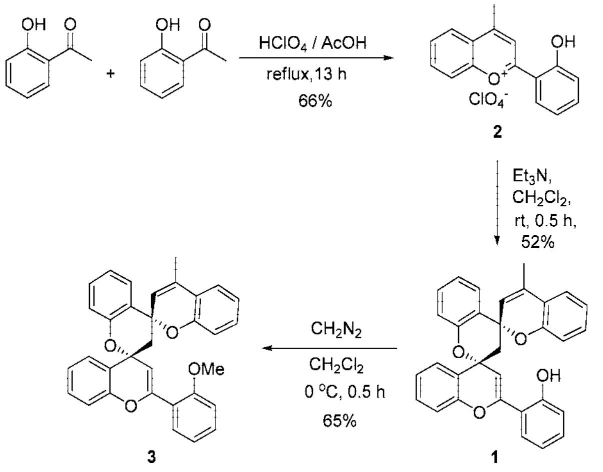
The thermochromic mechanism of Schiff bases containing a 2-hydroxyphenyl substituent has been reported to involve an intramolecular hydrogen transfer, producing the colored enol−keto tautomeric species[6g] (Scheme 1).

Scheme 1



For the past few decades, few new organic thermochromic molecular systems have been developed,[9] partly due to the fact that prediction of thermochromism from a given molecular structure remains infeasible. While extensive investigations have been carried out on thermochromisms of bis-spiropyrans[10] and bis-salicyl-Schiff bases,[11] no thermochromic colorant containing two different thermochromic skeletons has been reported. Combination of two different thermochromic functionalities presumably may generate compounds with unprecedented properties. Here, we introduce a novel organic thermochromic colorant **1** by incorporating an *o*-hydroxyphenyl substituent onto the enol ether of the spiropyran structure. This should serve to act in a similar way as the salicyl-Schiff base colorants. The thermochromic behaviors of the designed compound were explored by UV−vis spectroscopy, X-ray diffraction analysis, and variable-temperature NMR spectroscopy. A plausible thermochromic mechanism was proposed on the basis of the experimental results.

Scheme 2



Scheme 2 shows the two-step synthesis of the designed compound **1**. It started with an acid-mediated self-condensation of commercially available 2-hydroxyacetophenone to form a green flavylium salt **2**[12] followed by treating **2** with triethylamine in methylene chloride at room temperature to afford the spiropyran **1**. The structure of **1** was confirmed by single-crystal X-ray diffraction analysis as presented in Figure 1,[13] which clearly reveals two connected spiropyran

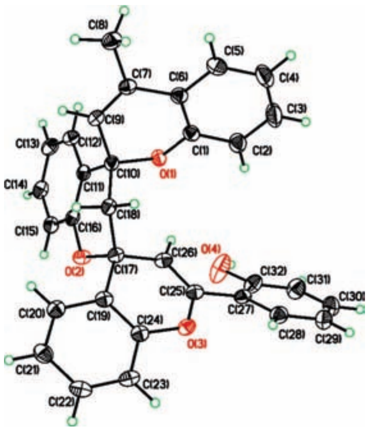


Figure 1. ORTEP crystal structure of **1**.

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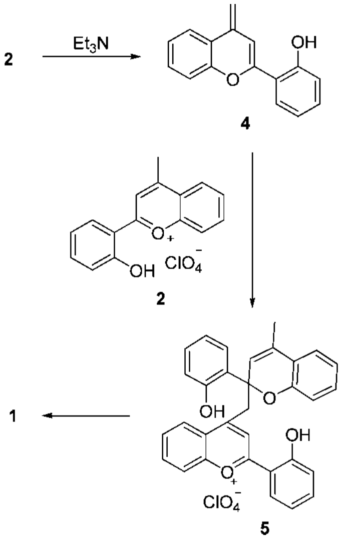
moieties. Note that the construction of the spiropyran **1** is highly atom-economical, with a total mass loss of only 38 g/mol from four molecules of 2-hydroxyacetophenone.

Scheme 3



Scheme 3 depicts the proposed mechanism for the formation of **1** from **2**. It involved first deprotonation of 4-methyl hydrogen on flavylium salt **2** by triethylamine to give 2-(4-methylene-4*H*-chromen-2-yl)phenol (**4**) followed by coupling with **2** to afford the intermediate **5**. Final intramolecular cyclization of **5** furnished the spiropyran **1**.

With compound **1** in hand, its thermochemical properties were then investigated. The spiropyran **1** is colorless at −20 °C and turns purple as the temperature is increased. The color reverts swiftly to colorless when the temperature is decreased. Figure 2 shows the partial UV−vis absorption spectra of **1** in chloroform at temperatures between −20 and +50 °C (the full spectra are shown in Figure S1 in the Supporting Information). With temperature increase, a new absorption band with the peak wavelength around 560 nm gradually increased. Although an isosbestic point appeared to be lacking when the temperature was increased, the absorbance at 560 nm showed smooth, continuous growth and reached a plateau. When the temperature was decreased, the purple species in chloroform quickly decayed away with the disappearance, i.e., turning colorless, of the 560 nm band.

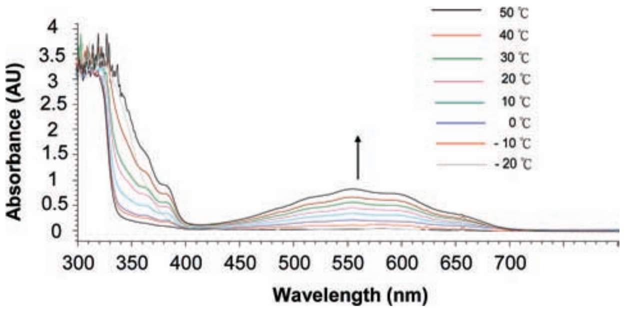
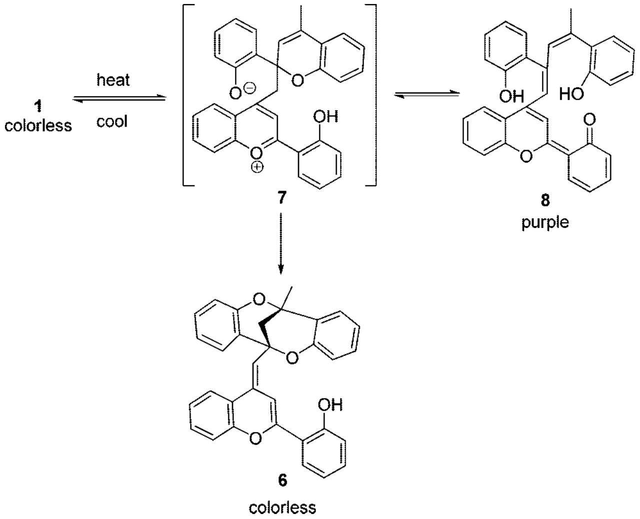


Figure 2. Partial UV−vis spectra of **1** (1.5×10^{-3} M in $CHCl_3$) at temperatures between −20 to +50 °C, with increments of 10 °C.

Scheme 4



Scheme 4 shows the proposed thermochromic switch of the spiropyran **1**. It involved a thermally induced heterolytic C−O bond cleavage of the spiropyran moiety to give the ring-opening zwitterionic species **7**. The subsequent intramolecular hydrogen transfer from the nearby 2-*o*-hydroxy group and isomeric ring opening of the second pyran ring afforded the purple enol−keto tautomeric species **8**. Although various attempts to isolate the product **8** proved to be futile, variable-temperature NMR experiments of **1** in $CDCl_3$ did provide the evidence for its emergence, that is, the observation of three new discernible singlets at 6.29, 5.21, and 4.78 ppm, which were tentatively assigned to the three olefin hydrogen absorptions of **8** (the spectra are showed in Figure S3 in the Supporting Information). In addition, formation of **8** could also be indirectly inferred by identification of the dioxabicycle **6** during the thermochromic process (Scheme 4). Figure 3 shows the X-ray crystal structure of **6**, which displays a rigid bicyclo[3. 3. 1] skeleton.[13] Isolation of the dioxabicycle **6** demonstrates that the thermally induced ring-opening intermediate **7** can undergo either a reversible intramolecular hydrogen transfer and then isomeric ring-opening of the

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(13) Crystallographic data (excluding structure factors) for **1** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-714538 and -714539, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

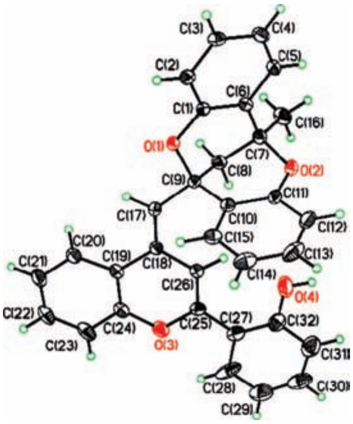

Figure 3. ORTEP crystal structure of **6**.

pyran ring to the purple enol−keto tautomeric species **8** or an irreversible intramolecular cyclization and subsequent isomerization to the colorless dioxabicycle **6** (Scheme 4). Presumably, the formation of **6** can be prevented by removal of the 4-methyl-2*H*-chromene moiety on **1**.

Compound **1** was converted to the corresponding *O*-methylated product **3**by treating it with diazomethane to determine whether the *o*-hydroxy group is required for the thermochromism (Scheme 2). The fact that compound **3** failed to exhibit any thermochromic property even under vigorous heating conditions indicates that the *o*-hydroxy group of **1** is essential for the observation of thermochromism. This study demonstrates that salicyl-Schiff base's imine can be substituted with other appropriate functionality without hampering its thermochromic properties, as long as the replaced group can provide a negative charge for intramolecular hydrogen transfer upon heating. Compared with the reported thermochromic properties of the salicyl-Schiff base colorants, this newly developed compound **1** has (1) a much lower enol−keto equilibrium constant (<0.01) at room temperature, probably because it needs an extra step (the ring-opening C−O bond cleavage) to initiate the thermochromism; (2) has sharper contrasts when the color changes, since **1** is colorless due to the lack of a nitrogen atom; and (3) has narrower temperature ranges of color-switching. Thus, we introduce here a new thermochromic colorant with an *o*-hydroxyphenyl-containing spiropyran skeleton. To the best of our knowledge, this represents the first example of a thermochromic colorant to exhibit salicyl-Schiff base-like thermochromic properties that does not contain an imine functional group in the molecule. We believe this hybrid design strategy may open an avenue for future development of the organic thermochromic dyes with new molecular structures.

In summary, a novel *o*-hydroxyphenyl-containing spiropyran **1** was designed and synthesized from 2-hydroxyacetophenone in two steps to study its thermochromic properties. This compound is sensitive to temperature and has a reversible color change with temperature variation. We have demonstrated that a new thermochromic colorant can be realized via combination of two different thermochromic skeletons, with suitable modifications, into a single molecular structure. Application of this hybrid strategy in design of new thermochromic dyes with novel molecular skeletons is currently in progress.

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Supporting Information Available: Synthesis of compounds **1**−**3**, experimental details, and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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