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Solvent effect on the thermochromism of new betaine dyes

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ABSTRACT

In the present study, five betaine dyes, BT1, BT2, BT3, BT4 and BT5 were successfully synthesized and fully characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS, IR and UV–Visible spectroscopy. Except BT5, remaining betaine dyes are newly synthesized. The reversible thermochromic properties of these dyes were investigated at different temperatures in different solvents. The large thermochromic effect was observed for the dyes and it was attributed to a combination of conformational changes coupled with the relative permittivity of the respective solvent. The thermochromic properties of the betaines were evaluated by UV–Vis studies, and DFT calculations were conducted to rationalize the dye structures. Finally this is the first attempt of the study of color changes in numerous solvents at different temperatures.

1. Introduction

Thermochromism refers to the reversible thermotransformation of a chemical species among two forms that possess different absorption spectra. Recently, thermochromic materials have received great interest due to the significant changes in their absorption and/or fluorescent properties in reaction to external stimulation, yielding numerous potential applications in a number of industries such as inks, paints, plastics, and textiles. Because of their temperature-sensitive nature, these materials are widely used in devices such as thermal indicators, tunable light filters, optical storage devices, chemo/biosensors, and other luminescent switches [1–7]. Until now, fluorans [8,9], conjugated polymers [10], betaines [11], spiropyrans [12,13], crystal violets [14] and inorganic compounds [15] have been extensively used as thermochromic dyes.

Among these dyes, betaine dyes are known as an interesting family of zwitterion compounds, whose UV–Vis spectra are rather sensitive to their environment. A number of betaines have been investigated for their different applications in thermochromism. Thermochromic properties were observed due to a temperature-induced differential desolvation of the highly zwitterionic ground state relative to its less dipolar first excited state [16]. Betaine dye systems have been evaluated for use in thermochromic responsive elastic polymer substrates [17], chromogenic materials [18] and thermochromism in transparent hydrogels [19]. The thermosolvatochromism of pyridinium N-phenolates and other betaine dyes has been applied in the design of optochemical devices for the detection of ambient temperatures. Burt encapsulated betaine in a stable organic silica sol-gel matrix, which exhibited changes in color upon exposure to temperature changes. The response of the device was reversible with respect to changes in temperature [20].

Betaine dyes are thermochromic, which means that the longest-wavelength intramolecular charge transfer (ICT) visible absorption band of these dyes depends on the solution temperature [21]. Several years ago, the temperature-dependent UV–Vis spectrum, or thermochromism, of Reichardt's dye was analyzed in acetonitrile [22]; then, the thermochromism of 4-pyridiniophenolate was analyzed by John O. Morley and co-workers [11]. Additional new findings have been observed regarding the thermochromic property of betaines [23–26]. To rationalize the behavior of the betaine dye and its sensitivity against small changes in its molecular-microscopic environment, this class of zwitterionic dyes has been repeatedly and intensively studied. In the series of our thermochromic studies [27], here we synthesized 5 betaine dyes (BT1 to BT5) with the aim of changing the thermochromic property with

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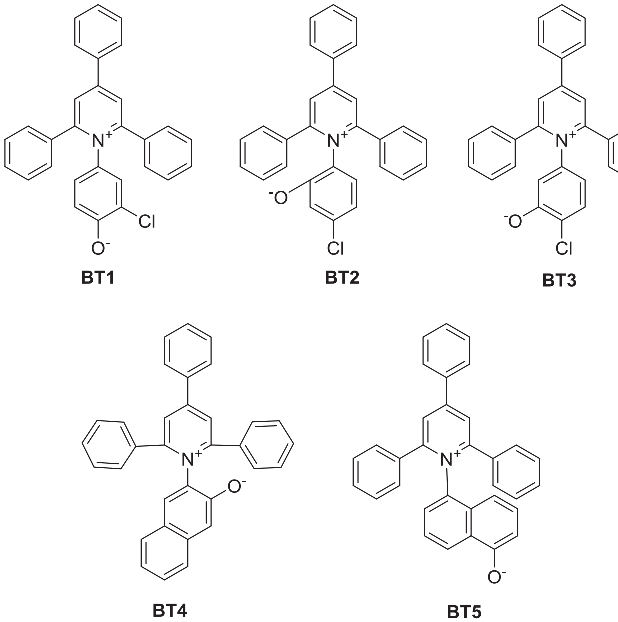


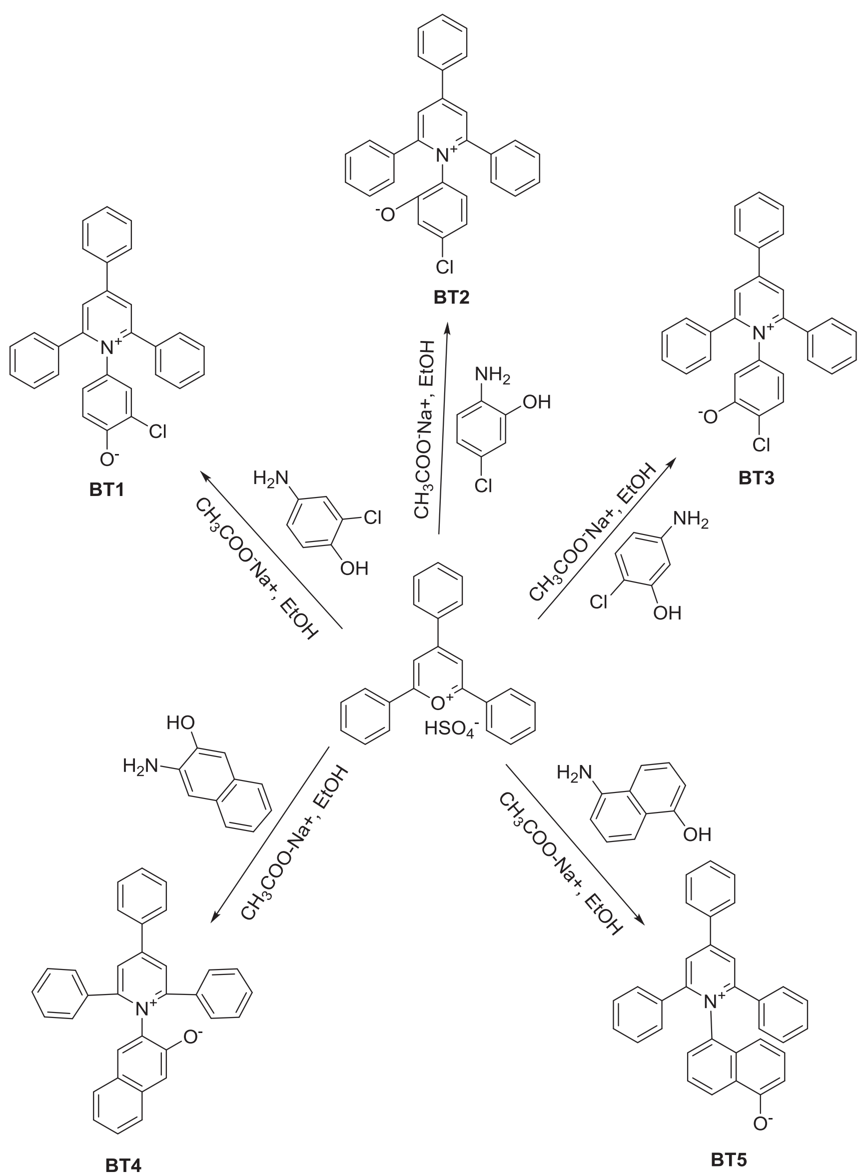
Fig. 1. Structures of the betaine dyes.

the variation in temperature. Except for 5-(2,4,6-triphenylpyridin-1-ium-1-yl)naphthalen-1-olate (BT4), remaining four betaine dyes were newly synthesized (Fig. 1). The synthesized betaines were fully characterized by ^{1}H NMR, ^{13}C NMR, IR and ESI-MS analysis. To gain further insight into the geometry, electronic structure, and optical properties of the dyes, we carried out thorough DFT and TDDFT calculations. The thermochromic properties of these compounds were studied in chloroform, ethanol, THF, toluene, benzene, xylene, DMF and acetonitrile, solvents with different temperature variations. Simply we discuss the thermochromic properties of all the betaines with respect to electronic effects. To date except BT5, no any reports are available for the synthesis of BT1, BT2, BT3 and BT4.

2. Experimental section

2.1. Chemicals, materials and instruments

All solvents and reagents (analytical and spectroscopic grades) were commercially obtained and used as received unless otherwise noted. An AVANCE III 600 spectrometer (Akishima, Japan) was operated at 600 MHz and 150 MHz for ^{1}H and ^{13}C NMR spectroscopy, respectively. DMSO-d_6 was used as the solvent, and Alice 4.0



Scheme 1. Synthetic route for the preparation of betaines BT1-BT5.