Dyes and Pigments 136 (2017) 458-466

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Solvent effect on the thermochromism of new betaine dyes



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ARTICLE INFO

Article history: Received 11 June 2016 Received in revised form 15 August 2016 Accepted 16 August 2016 Available online 18 August 2016

Keywords: Thermochromism Betaines Aminophenol Hypsochromic Reversible

ABSTRACT

In the present study, five betaine dyes, BT1, BT2, BT3, BT4 and BT5 were successfully synthesized and fully characterized by ¹H NMR, ¹³C 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.

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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-

* Corresponding author. E-mail address: youngason@cnu.ac.kr (Y.-A. Son). 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 longestwavelength 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 molecularmicroscopic 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 ¹H NMR, ¹³C 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 ¹H and ¹³C 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.



Fig. 2. (a) Color change of BT1 at 25 °C and -20 °C in a chloroform solution; (b) UV-Vis absorption spectra of BT1 in chloroform (1 × 10⁻³ M) at different temperatures.

software was used for analysis. The chemical shifts (δ values) are reported in ppm downfield from an internal standard (Me₄Si). ESI-Mass spectra were recorded on a 4000 Q TRAP mass spectrometer. FT-IR spectra were recorded on an ALPHA-P spectrometer. UV–Vis absorption spectra were recorded using an Agilent 8453 spectrophotometer.

2.2. Synthesis of betaines

2.2.1. General procedure for the synthesis of the betaine dyes

The preparation was carried out by modifications in the procedure [26] to that reported by Kessler and Wolfbeis. A mixture of 2,4,6-triphenylpyrylium hydrogen sulfate (2 mmol), aminophenol or aminonaphthol derivative (2 mmol), and anhydrous sodium acetate (6 mmol) were added to 5 mL of ethanol. The mixture was refluxed for 3 h and cooled. Next, 10 mL of a 5% aqueous sodium hydroxide solution was added, and the mixture was stirred for another 5 min. Then, 100 mL of water was added to the reaction mixture, which was then extracted with DCM (2 \times 50 mL). The combined organic layers were dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The resulting red crystals were recrystallized from aqueous ethanol and dried over P₂O₅ under vacuum for 24 h.

2.2.2. 2-chloro-4-(2,4,6-triphenylpyridin-1-ium-1-yl)phenolate (BT1)

Yield: (0.779 g, 90%), mp 205–207 °C. ¹H NMR (600 MHz, DMSO- d_6): δ 8.48 (s, 2H), 8.24–8.32 (m, 2H), 7.60–7.69 (m, 3H), 7.37–7.49 (m, 10H), 6.90 (d, J = 2.6 Hz, 1H), 6.54–6.60 (m, 1H), 5.84 (d, J = 8.8, 1H) ppm; ¹³C NMR (150 MHz, DMSO- d_6): δ 157.1, 153.9,

134.0, 133.6, 129.6, 129.5, 129.4, 128.5, 128.0, 127.5, 125.1, 121.4, 117.7. IR ν_{max} in cm⁻¹ (KBr): 3020, 1619, 1575, 1492, 1214, 745, 668; ESI-MS: 433 [M]⁺.

2.2.3. 5-chloro-2-(2,4,6-triphenylpyridin-1-ium-1-yl)phenolate (BT2)

Yield: (0.757 g, 87.5%), mp 201–203 °C. ¹H NMR (600 MHz, DMSO- d_6): δ 8.42 (s, 2H), 8.23–8.27 (m, 2H), 7.56–7.67 (m, 7H), 7.33–7.42 (m, 6H), 6.68 (d, J = 8.2 Hz, 1H), 5.86–5.89 (m, 1H), 5.52 (d, J = 8.2, 1H) ppm; ¹³C NMR (150 MHz, DMSO- d_6): δ 158.1, 154.7, 135.0, 134.3, 134.2, 132.4, 130.2, 130.0, 129.8, 129.4, 129.1, 128.4, 128.1, 125.6, 120.0 ppm; IR ν_{max} in cm⁻¹ (KBr): 3020, 1619, 1587, 1555, 1483, 1214, 745, 668; ESI-MS: 433 [M]⁺.

2.2.4. 2-chloro-5-(2,4,6-triphenylpyridin-1-ium-1-yl)phenolate (BT3)

Yield: (0.792 g, 91.5%), mp 199–201 °C. ¹H NMR (600 MHz, DMSO- d_6): δ 8.48 (s, 2H), 8.26–8.32 (m, 2H), 7.52–7.70 (m, 7H), 7.37–7.46 (m, 6H), 6.65 (d, J = 8.1 Hz, 1H), 6.02–6.10 (m, 1H), 5.84 (d, J = 8.1, 1H) ppm; ¹³C NMR (150 MHz, DMSO- d_6): δ 156.4, 155.0, 138.6, 134.0, 132.6, 130.2, 130.0, 129.9, 129.2, 128.3, 127.8, 125.7, 119.2 ppm; IR v_{max} in cm⁻¹ (KBr): 3020, 1618, 1598, 1578, 1480, 1412, 1214, 749, 667; ESI-MS: 433 [M+H]⁺.

2.2.5. 3-(2,4,6-triphenylpyridin-1-ium-1-yl)naphthalen-2-olate (BT4)

Yield: (0.776 g, 86.5%), mp 191–194 °C. ¹H NMR (600 MHz, DMSO- d_6): δ 8.45 (s, 2H), 8.33 (s, 2H), 8.26–8.31 (m, 2H), 7.62–7.73 (m, 6H), 7.24–7.31 (m, 6H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.18 (s, 1H) ppm;



Fig. 3. (a) Color change of BT2 at 25 °C and -20 °C in a chloroform solution; (b) UV-Vis absorption spectra of BT2 in chloroform (1 × 10⁻³ M) at different temperatures.



Fig. 4. (a) Color change of BT3 at 50 °C, 20 °C and -20 °C in a chloroform solution; (b) UV-Vis absorption spectra of BT3 in chloroform (1 × 10⁻³ M) at different temperatures.



Fig. 5. (a) Color change of BT4 at 25 °C and -20 °C in a chloroform solution; (b) UV-Vis absorption spectra of BT4 in chloroform (1 × 10⁻³ M) at different temperatures.



Fig. 6. (a) Color change of BT5 at 50 °C and -10 °C in a chloroform solution; (b) UV–Vis absorption spectra of BT5 in chloroform (1 × 10⁻³ M) at different temperatures.

¹³C NMR (150 MHz, DMSO-*d*₆): δ 157.2, 154.5, 134.3, 134.1, 132.4, 130.2, 130.0, 129.6, 129.1, 128.1, 125.5, 124.1, 110.5 ppm; IR ν_{max} in cm⁻¹ (KBr): 3020, 1619, 1554, 1469, 1214, 745, 668; ESI-MS: 449 [M]⁺.

2.2.6. 5-(2,4,6-triphenylpyridin-1-ium-1-yl)naphthalen-1-olate (BT5)

Yield: (0.74 g, 82.5%), mp 196–198 °C. ¹H NMR (600 MHz, DMSO- d_6): δ 8.67 (s, 2H), 8.36–8.41 (m, 2H), 8.03 (d, J = 8.2 Hz, 1H), 7.65–7.73 (m, 3H), 7.61 (d, J = 7.1 Hz, 1H), 7.36–7.42 (m, 4H), 7.16–7.28 (m, 7H), 7.08 (t, J = 8.2 Hz, 1H), 6.24 (d, J = 6.5 Hz, 1H),

6.00 (d, J = 6.5 Hz, 1H) ppm; ¹³C NMR (150 MHz, DMSO- d_6): δ 156.9, 155.7, 133.7, 133.5, 132.7, 132.5, 130.6, 130.4, 129.9, 129.6, 129.0, 127.5, 126.8, 125.6, 119.0, 109.6 ppm; IR ν_{max} in cm⁻¹ (KBr): 3021, 1618, 1544, 1214, 745, 668; ESI-MS: 449 [M+H]⁺.

2.3. Computational details

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed on all of the betaine dyes. All the calculations reported in this paper were carried out at the B3LYP level using 6-31G** basis set using Gaussian 09 program [28].



Fig. 7. Color change of BT1-BT5 at -20 °C, 20 °C and 60 °C in different solvents (a) at 1×10^{-4} M and (b) at 1×10^{-3} M concentration.

The geometry optimization of the two dyes was carried out using the M06 [29] hybrid meta exchange correlation density functional at the 6-31G (d,p) level of theory. During the geometry optimization, we did not impose any symmetry constraints. The frequency analysis was carried out on optimized geometries to confirm that each configuration is indeed a minimum on the potential energy surface. We obtained the electron density distribution isosurfaces of the dyes by performing a population analysis. To characterize the photophysical properties of the betaine dyes, we performed TDDFT simulations on the optimized ground state structures.

3. Results and discussion

3.1. Synthesis of the betaine dyes

We synthesized 5 betaine dyes, all of which were newly synthesized except BT5. The synthetic protocol for the preparation of the target dyes BT1, BT2, BT3, BT4 and BT5 is shown in Scheme 1. 2,4,6-Triphenylpyrylium hydrogen sulfate was prepared according to the literature procedure [30]. The betaine dyes were prepared using a previously reported procedure [26], with slight modifications. One equivalent of 2,4,6-triphenylpyrylium hydrogen sulfate, aminophenol or amino naphthol and 3 equivalents of anhydrous sodium acetate were dissolved in ethanol. Here, after completion of the reaction, aqueous NaOH was added, and the solution was directly extracted with DCM. All compounds were recrystallized in aqueous ethanol. Finally, the synthesized dyes were fully characterized by ¹H NMR, ¹³C NMR, IR, and ESI-Mass spectrometry, as well as UV–Vis absorption spectrometry.

3.2. Absorption and thermochromic studies in chloroform

The effects of solvent on electron transfer receive continuous attention in the field of physical chemistry and are conveniently studied spectroscopically [31]. Here, we conducted UV–Vis studies in chloroform at different temperatures. All the dyes showed a reversible color change. Dye BT1 at ambient temperature was blue in color, and its absorption maximum was located at 630 nm. When



Fig. 8. Optimized ground state (S₀) geometries of the betaines obtained at the DFT level using a B3LYP/6-31G** basis set.

Table 1
Energies of the frontier molecular orbitals calculated at the DFT level using a B3LYP/
6-31G ^{**} basis set, along with the optical band gap (E_{0-0}) .

Dye	E _{HOMO} (eV)	E _{LUMO} (eV)	$E_{0-0} (eV)^{a}$
BT1	-4.371	-2.666	1.705
BT2	-4.367	-2.625	1.742
BT3	-3.894	-2.579	1.315
BT4	-3.668	-2.773	0.895
BT5	-3.882	-2.884	0.998

the temperature was changed to -20 °C, its absorption maximum hypsochromically shifted (575 nm) in color to red (Fig. 2). The original position of the absorption maximum and the blue color were quickly restored upon warming to room temperature, and this reversible thermochromic process was repeated a number of times without significant changes in the UV–Vis spectra. A hypsochromic (blue) shift is observed for molecules whose dipole moment decreases in the excited state compared to the ground state, stabilizing the ground state energy in polar solvents; this phenomenon is called negative solvatochromism and is often observed for molecules with $n \rightarrow \pi^*$ transitions [32,33]. The color transition with temperature is explained by the small energy gap between the conformers. The alteration in the color of the dye with varying temperature is supportive, suggesting that the more stable conformers predominate at low temperatures [11].

In the case of BT2 in chloroform, the absorption maximum changed from 575 nm at 25 °C to 515 nm at -20 °C with an associated color change from purple to red (Fig. 3). The absorption maximum of BT3 in chloroform moved from 570 nm at room temperature to 520 nm when the solution was cooled to -20 °C with a change in color from red to blue, whereas the absorption

maximum bathochromically shifted to 595 nm with a color change to green when the temperature was increased to 50 °C (Fig. 4). In BT4, the absorption maximum changed from 602 nm at 25 °C to 560 nm at -10 °C with an associated color change from green to reddish brown (Fig. 5). Finally, BT5 showed an absorption maximum at 680 nm at 50 °C accompanied by a yellow color, and upon changing the temperature to -10 °C hypsochromically shifted the maximum to 550 nm with greenish yellow (Fig. 6). The explanation for the hypsochromic shift of the all the dyes observed upon cooling, or the thermochromic behavior, is attributable, at least in part, to the increase in the relative permittivity of the solvent with decreasing temperature also with combination of dielectric effect and a hydrogen bonding effect [11]. In Figs. 2-6, we observed that lower temperatures exhibit very high backgrounds in those wavelength regions where no absorbance would be expected $(\lambda > 750 \text{ nm})$ and the backgrounds keep increasing with decreasing temperature. This anomalous UV-Visible absorption could be due to the scattered light effect.

This result reveals that the nature of the substituent present on the betaine molecule has a significant role in the solution, and we observed that the spectrum red shifts with increasing temperature.

3.3. Thermochromic properties of BT1-BT5 in different solvents

Betaine dyes are solvatochromic in nature [31,34]. The S_0 - S_1 electronic transition blue shifts with increasing solvent polarity as a result of the much larger dipole moment of betaines in the ground state compared to the excited state [35,36]. Here, all betaine dyes showed different color properties, and these dyes were evaluated for their thermochromic behavior in 10^{-3} and 10^{-4} M solutions of acetonitrile, DMF, xylene, benzene, EtOH, CHCl₃, toluene, and THF (Fig. 7). The thermochromic behavior of these betaine dyes was



Fig. 9. Electron density distribution in HOMO-1, HOMO, LUMO, and LUMO+1 for the betaines obtained at the DFT level using a B3LYP/6-31G** basis set.

Table 2

Simulated absorption wavelengths (λ_{cal}), oscillator strengths (f), and coefficients of configuration interaction (CI) with the dominant contribution to each transition of the five dyes.

Dye	Transition	$\lambda_{cal} (nm)$	$\lambda_{exp}^{a}\left(nm ight)$	f	CI coefficient	Dominant contribution (%) ^b
BT1	$S_0 \rightarrow S_1$	740		0.3097	0.55916	$H \rightarrow L(62)$
	$S_0 \rightarrow S_2$	631	630	0.0002	0.69375	$H-1 \rightarrow L(96)$
	$S_0 \rightarrow S_3$	602		0.0253	0.69260	$H \rightarrow L+1$ (96)
	$S_0 \rightarrow S_4$	429		0.0098	0.69145	$H-2 \rightarrow L(96)$
	$S_0 \rightarrow S_5$	408		0.0309	0.69114	$H \rightarrow L+2$ (96)
BT2	$S_0 \rightarrow S_1$	1171		0.0005	0.70305	$H \rightarrow L(99)$
	$S_0 \rightarrow S_2$	668		0.0040	0.70209	$H-1 \rightarrow L(99)$
	$S_0 \rightarrow S_3$	586	575	0.0004	0.70205	$H \rightarrow L+1$ (99)
	$S_0 \rightarrow S_4$	466		0.0065	0.70136	$H-2 \rightarrow L(98)$
	$S_0 \rightarrow S_5$	432		0.0005	0.70530	$H-1 \rightarrow L+1 (99)$
BT3	$S_0 \rightarrow S_1$	2642		0.0085	0.64406	$H \rightarrow L(83)$
	$S_0 \rightarrow S_2$	956		0.0033	0.62953	$H-1 \rightarrow L(79)$
	$S_0 \rightarrow S_3$	846		0.0390	0.61050	$H \rightarrow L+1$ (75)
	$S_0 \rightarrow S_4$	561	570	0.0007	0.70397	$H-1 \rightarrow L+1 (99)$
	$S_0 \rightarrow S_5$	537		0.0332	0.68816	$H-2 \rightarrow L(95)$
BT4	$S_0 \rightarrow S_1$	1713		0.0000	0.70367	$H \rightarrow L(99)$
	$S_0 \rightarrow S_2$	734		0.0040	0.70161	$H-1 \rightarrow L(98)$
	$S_0 \rightarrow S_3$	703		0.0002	0.70279	$H \rightarrow L+1$ (99)
	$S_0 \rightarrow S_4$	554	602	0.0033	0.70051	$H-2 \rightarrow L(98)$
	$S_0 \rightarrow S_5$	466		0.0001	0.67569	$H \rightarrow L+3 (91)$
BT5	$S_0 \rightarrow S_1$	1906		0.0566	0.50073	$H \rightarrow L(50)$
	$S_0 \rightarrow S_2$	873		0.0129	0.65949	$H \rightarrow L+1$ (87)
	$S_0 \rightarrow S_3$	817	680	0.0226	0.66098	$H-1 \rightarrow L(87)$
	$S_0 \rightarrow S_4$	525		0.0231	0.68488	$H \rightarrow L+2$ (94)
	$S_0 \rightarrow S_5$	493		0.0009	0.69678	$H \rightarrow L+3 (97)$

^a Experimental absorption wavelengths in CHCl₃.

^b H and L denote HOMO and LUMO, respectively.

assessed at three different temperatures (-20 °C, 20 °C, 60 °C). All five dves showed good color variation in the different solvents. In the 10^{-3} M solutions of the dyes, we obtained good thermochromic color change properties compared to the 10^{-4} M solutions, and we also observed a change in the thermochromic properties with changes in the solvent polarity. Here, by changing from aprotic to protic solvents, the completely different thermochromic colors observed for all the dves may have resulted from the strong hydrogen bonding between the acidic hydrogen of the solvent and the electronegative oxygen of betaine [37]. According to this figure, we achieved almost all colors with thermochromic properties with these five dyes. According to Morley and Padfield theoretical calculations the molecular structure of betaine using the PM3/COSMO method, a clockwise and anticlockwise conformational mobility of the pendant phenyl groups relative to the pyridinium center, and the thermosolvatochromic behavior of betaine in solvent is a result of the combination of changes in the conformational profile of the dye and of the alterations in the relative permittivity of the solvent with changes in the temperature [11]. To the best of our knowledge, this is the first attempt of a study that evaluates the color changes in numerous solvents at different temperatures.

3.4. Computational studies

To gain further insight into the geometry, optical properties, and electronic structure of these betaine dyes, we carried out in-depth DFT and TDDFT calculations. The optimized ground-state geometries of the dyes are shown in Fig. 8.

The calculated molecular orbital energy levels are given in Table 1. As shown in Fig. 9, the simulated HOMO energies of BT1, BT2, BT3, BT4 and BT5 are -4.37, -4.36, -3.89, -3.66 and -3.88 eV, respectively. The TDDFT first transition energies ($S_0 \rightarrow S_1$) were considered the optical bandgaps of the dyes, which were 1.70, 1.74, 1.31, 0.89 and 0.99 eV for BT1, BT2, BT3, BT4 and BT5, respectively. In the present study, we calculated the LUMO energy by taking the sum of the HOMO energy and the TDDFT transition energy, rather

than from the unreliable Kohn-Sham LUMO eigenvalue. The obtained LUMO energies of BT1, BT2, BT3, BT4 and BT5 are -2.66, -2.62, -2.57, -2.77 and -2.88 eV, respectively.

The UV–Vis spectra of all the dyes were simulated, and the TDDFT simulations reproduced the main bands observed in the experimental UV–Vis spectra. The first five singlet vertical excitation energies calculated along with their oscillator strengths are given in Table 2. The calculated absorption maxima in the low-energy region of the BT1, BT2, BT3 and BT4 dyes are located at 631, 586, 561 and 554, respectively, which agree well with the experimental results. Whereas in the case of BT5, the large difference between experimental (680 nm) and theoretical (817 nm) absorption maxima may be due to the intermolecular interactions which the theoretical methods cannot take into account [38]. These low-energy absorptions mainly occur from the transition from HOMO to LUMO of the dyes. The excitation energies and oscillator strengths were interpolated by a Gaussian convolution with an FWHM of 2500 cm⁻¹.

4. Conclusion

The outstanding sensitivity of the long-wavelength, intramolecular charge-transfer UV–Vis absorption of the pyridinium-N phenoxide betaine dyes to small changes in solvent polarity and solution temperature was demonstrated. Here, small changes induced greater chromic effects, showing that betaine dyes are very sensitive towards small changes in molecular structure. Furthermore, this paper demonstrates that the pyridinium unit can function as a basic skeleton and phenyl moieties can be modified with different substituents to produce promising compounds for new functional betaine dyes. Substitution on the phenyl group affects the development of the color formation reaction in the solution state. We report herein color changes in chloroform from ambient temperature to -20 °C as follows: BT1, blue to red; BT2, purple to red; BT3, red to blue; BT4, green to reddish-brown; and BT5, yellow to greenish-yellow.

Acknowledgement

This study was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (Grant no. 2015063131).

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