

Studies on the synthesis and thermochromic properties of crystal violet lactone and its reversible thermochromic complexes

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Abstract

In this article, a crucial compound, crystal violet lactone (CVL), was prepared by the reaction of *N,N*-dimethylaniline, *p*-dimethylanilino-benzaldehyde and *m*-dimethylanilino-benzoic acid. Taking alcohols or carboxylic acids as solvents, 15 novel reversible thermochromic complexes were prepared by means of chelation reaction between electron donor CVL and electron acceptor such as various phenols, aromatic amines, carboxylic acids, and Lewis acids, respectively. The structure of CVL is characterized by ¹H NMR and MS. The reversible thermochromic behavior of these compounds are studied by DSC/TG, IR, and Raman spectrum. Results indicate that mechanism of these reversible thermochromic complexes is the lactone ring tautomerism when the temperature is low or high. Thermochromic color degree of these complexes is dependent on the acidity of electron acceptor and thermochromic temperature is dependent on the properties of solvent compounds. The properties of electron acceptor and solvent compounds also determined the thermochromic process of the complexes, which followed the first-order kinetic equation, and the values of energy of activity (E_a) of thermochromic process are correlated with the components of the complexes nearly. The stronger the acidity of phenols is, and the deeper the thermochromic color degree is, the higher the value of E_a is, when electron acceptors are phenols.

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1. Introduction

A thermochromic compound change color when heated and revert to the original on cooling. This reversible dependence of color on temperature is known as thermochromic property. The use of thermochromic material has been discussed in lecture demonstration [1–3]. Organic reversible thermochromic complexes are increasingly important in recent years in the study and used for textiles and smart coating. Especially, organic complexes with a leuco dye (electron donor), a weak acid (electron acceptor), and a solvent are commonly used in consumer application [4–6], because the temperature at which they change color can be presented within the life-environment temperature range. They can be used as thermochromic coloring agents for toys, temperature indicators for plastic and printing inks, for paints and so forth [7,8]. In the past decade, although

many of complexes from crystal violet lactone (CVL) are reported for three component thermochromic dye mixtures [9,10] and thermochromic mechanism of their operation is not yet known definitively. The present work describes alcohol or carbonic acid as solvent compound, and various phenols or aromatic amines or carboxylic acids or Lewis acids as electron acceptor, respectively. Fifteen novel reversible thermochromic complexes were prepared from central compound CVL. Relations between the structure and properties of these complexes were confirmed and the values of E_a of thermochromic peaks of the complexes were calculated by kinetic equation of thermochemistry.

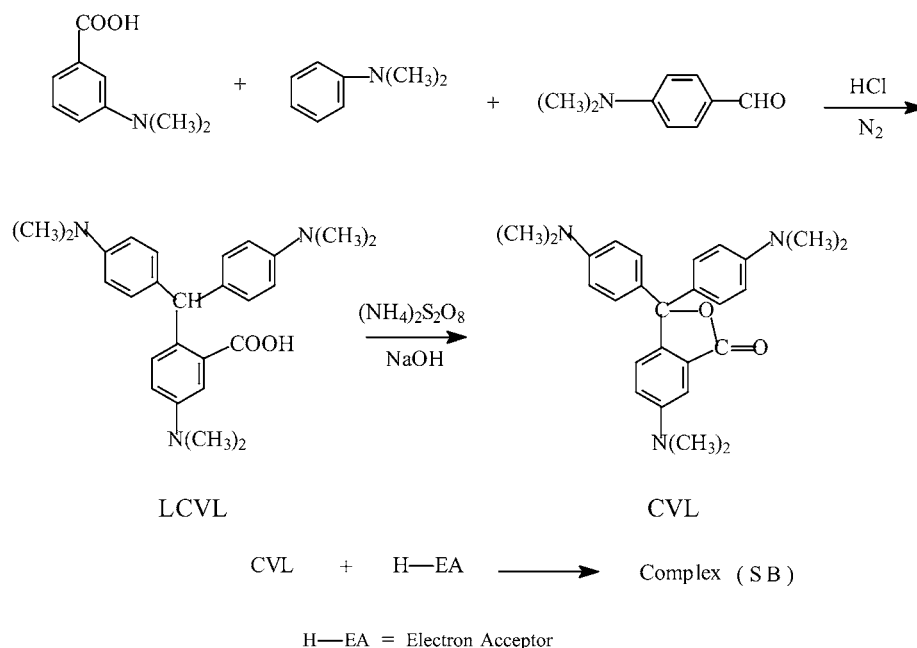
2. Experimental

2.1. Materials

All chemicals used are of chemical or analytic grade, and used without further purification. CVL was synthesized as showed in [Scheme 1](#).

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Scheme 1.

CVL was prepared by direct condensation of the *m*-dimethylaminobenzoic acid with *p*-dimethylamino benzaldehyde. *N,N*-Dimethylaniline was dissolved in hydrochloric acid with a slight excess of urea and refluxed for 6 h under the protection of nitrogen. After neutralization with sodium hydroxide solution, leuco crystal violet lactone (LCVL) was precipitated and filtered from the solution.

Followed LCVL was dissolved in sodium hydroxide solution with 8% molar of ferrous sulfate and 10% molar of

pyridine, and refluxed for 8 h at 75 °C. The precipitates were filtered and washed with water thrice and gave pale yellow sediment [11]. MS, IR, ¹H NMR, and melting points were utilized to establish the purity of the compounds.

The CVL was dissolved in melting solvent, and then various phenols, aromatic amines, carboxylic acids, or Lewis acids added and heated to about 110 °C slowly. Keeping the solution at 110 °C for 2 h, then cooling it to room temperature, a reversible thermochromic complexes were obtained. The results are shown in Table 1.

Table 1
Compositions and thermal behavior of these complexes under investigation

SB	Composition ^a		Property	Color change ^b
	Electron acceptor	Solvent compound		
(I)	Cresol red	Octadecanol	Thermochromic	Earthyellow \rightleftharpoons red brown
(II)	<i>p</i> -Dihydroxybenzene	Hexadecanol	Thermochromic	Pale blue \rightarrow colorless \leftarrow deep blue \leftarrow pale blue
(III)	Tannic acid	Octadecanol	Thermochromic	Blue \rightleftharpoons colorless
(IV)	Methyl propyl phenol	Octadecanol	Thermochromic	Blue purple \rightleftharpoons colorless
(V)	Methyl propyl phenol	Hexadecanol	Thermochromic	Blue \rightleftharpoons colorless
(VI)	Phenolpropenoic acid	Octadecanol	Thermochromic	Blue green \rightleftharpoons colorless
(VII)	<i>p</i> -Methylphenol	Hexadecanol	Thermochromic	Deep blue \rightleftharpoons colorless
(VIII)	<i>p</i> -Methylphenol	Octadecanol	Thermochromic	Deep blue \rightleftharpoons colorless
(IX)	Phenolphthalein	Hexadecanol	Thermochromic	Blue purple \rightleftharpoons colorless
(X)	<i>m</i> -Nitrobenzoic acid	Octadecanol	Thermochromic	Blue \rightleftharpoons colorless
(XI)	Propyl gallate	Octadecanol	Thermochromic	Blue \rightleftharpoons colorless
(XII)	Calcium chloride	Octadecanol	Thermochromic	Pale blue \rightarrow colorless \leftarrow blue purple \leftarrow pale blue
(XIII)	Calcium chloride	Stearic acid	Thermochromic	Pale blue \rightleftharpoons colorless
(XIV)	<i>m</i> -Aminobenzoic acid	Octadecanol	Thermochromic	Pale blue \rightleftharpoons colorless
(XV)	MgCl ₂ ·6H ₂ O	Stearic acid	Thermochromic	Blue green \rightleftharpoons colorless
(XVI)	Magnesium sulfate	Octadecanol	Nonthermochromic	White
(XVII)	NiCl ₂ ·6H ₂ O	Octadecanol	Nonthermochromic	Blue

^a The mass ratio of CVL, electron acceptor, and solvent is 1:20:40.

^b \rightarrow , heating; \leftarrow , cooling.

2.2. Analysis and measurement

The IR spectra was recorded in KBr on FT-8000 spectrometre. The ^1H NMR spectra and MS were recorded on JOEL-FX-90MHz spectrometer using CDCl_3 as solvent and tetramethylsilane as internal reference and HP-5988A spectrometer, respectively. The DSC spectra and TG spectra were recorded on Perkin-Elmer Pyris 1 spectrometre and RIGAKU TAS-100 spectrometre at a heating rate of $10^\circ\text{C}/\text{min}$ in helium, respectively.

3. Results and discussion

The compositions and thermochromic properties of these complexes are showed in Table 1. The DSC/TG diagrams of these complexes were recorded and their data are summarized in Fig. 1 and Table 2, respectively. The results can be classified into two sets: first, those heated below the melting point and then colored; and second, those heated until melting and then colored. The results shows that thermochromism is displayed as a color change: blue \rightleftharpoons

Table 2
DSC and E_a data of part of these complexes under investigation

SB	mp ($^\circ\text{C}$)	Transition temperature ($^\circ\text{C}$)	Peak temperature ($^\circ\text{C}$)	ΔH (J/g)	E_a (kJ/mol)
(I)	56	51	50.3, 52.9, 56.7	31.8, 6.8, 59.9	84.9, 32.7
(II)	45	43	45.1, 47.2	189.4, 5.9	161.9
(V)	48	35	47.6	188.8	79.3
(VII)	49	43	44.2	111.6	57.3
(IX)	49	38	43.6, 47.6	9.3, 57.0	142.7
(X)	53	45	47.9, 52.9	11.2, 83.2	26.3
(XI)	53	49	50.7, 55.6	50.5, 87.7	92.3
(XII)	67	35, 68	35.8, 59.3, 64.6	6.9, 0.8, 25.5	18.0, 34.5
(XIV)	56	51	51.3, 56.8	17.5, 29.4	66.3
(XV)	57	47, 54	54.0, 56.3	33.7, 28.0	112.5

colorless and earth-yellow \rightleftharpoons red brown. In the solid state via a thermal process, those complexes from SB(II)–(XIII) show the color changes blue \rightleftharpoons colorless and pale blue \rightarrow colorless \leftarrow deep blue \leftarrow pale blue, respectively. This can be explained in terms of thermal lactone ring tautomerism as showed in Scheme 2 [12,13].

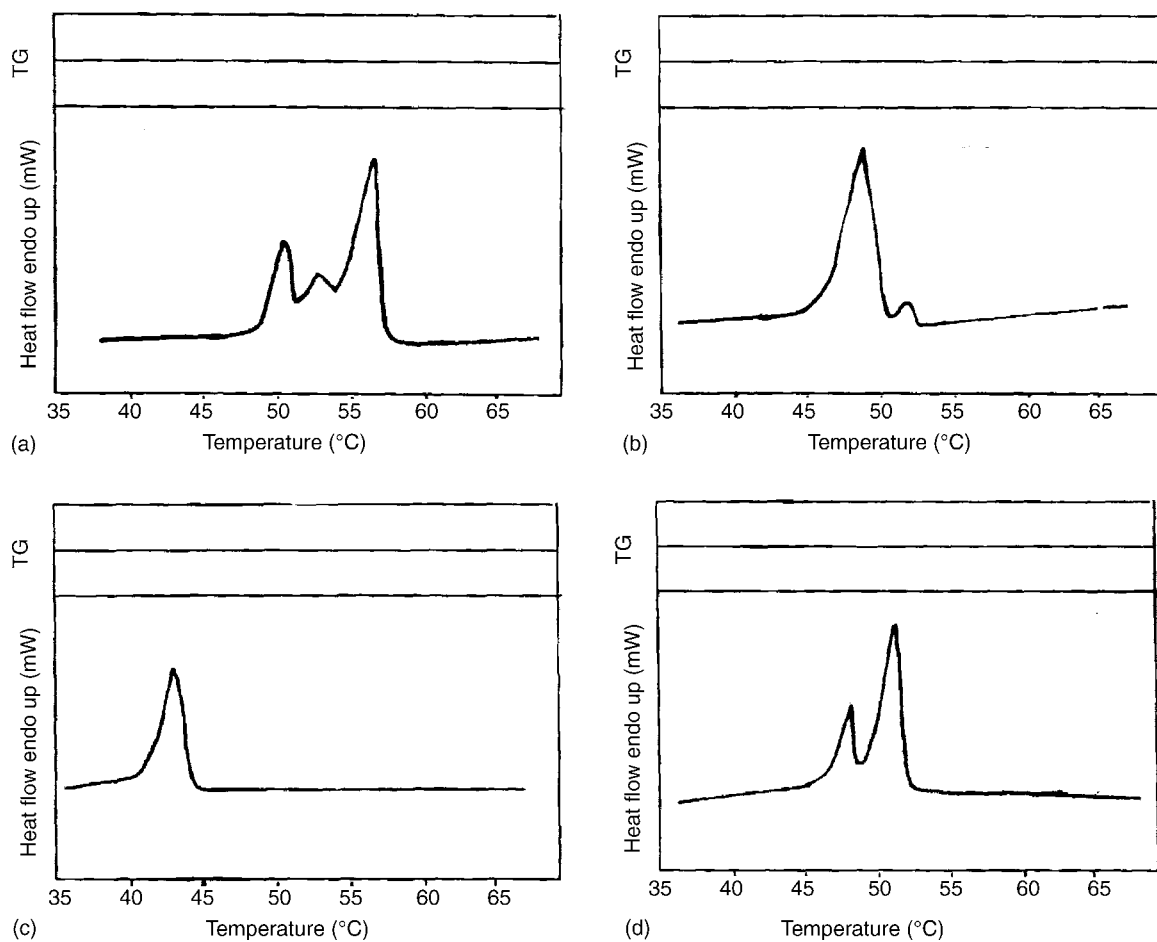
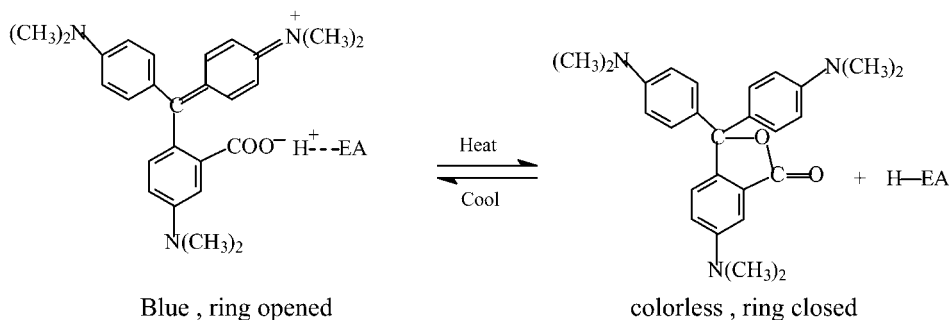


Fig. 1. DSC/TG curves of part of the reversible thermochromic complexes. (a) SB(I), (b) SB(II), (c) SB(VII), and (d) SB(XI). The samples weighed from 10–14 mg and the temperature varied from 20 to 100°C at a heating rate of $10^\circ\text{C}/\text{min}$ in helium.



Scheme 2.

As shown in the IR spectra, the peak of carbon–oxygen single bond weaken and some novel peaks come out when the complexes change their color at low temperature. The Raman spectra show that when the color changed, the Raman shifts of carbon–oxygen single bond move to higher frequencies in the structure of symmetrical oxygen–carbon–oxygen. The ^1H NMR spectra show that there existed combination action between the hydrogen of electron acceptor and the structure of symmetrical oxygen–carbon–oxygen, which can make the ring-opened structure stable with the action of solvent. Consequently, the complexes show the reversible color changes under the influence of temperature [14].

As shown in Table 1, all the complexes possess good reversible thermochromic behavior, short returning time, and high sensitivity. The variation of their colors show the two formats with the variation of temperature, one is single-color reversible thermochromism such as SB(IV), (V), (VI), etc., the other is multi-color reversible thermochromism such as SB(II), (XII), (XIV), etc. When the complexes possess the same electron acceptor and the different solvent, their thermochromic temperature are obviously different. For example, the thermochromic temperature of SB(IV) is 41°C , while the thermochromic temperature of SB(V) is 35°C . This indicate that the melting points of solvent controls the temperature at which the color change will take place. As far as the complexes having the same solvent and the different electron acceptor are concerned, their thermochromic color degree and process are obviously different. For example, the thermochromic color change of SB(VIII) is deep blue \rightleftharpoons colorless, while the thermochromic color change of SB(XIV) is pale blue \rightleftharpoons colorless, the thermochromic process of SB(II) is pale blue \rightarrow colorless \leftarrow deep blue \leftarrow pale blue, while the thermochromic process of SB(IX) is blue purple \rightleftharpoons colorless. These result illustrated that the electron acceptor of complexes have effect on their the thermochromic color degree such as SB(V) and (VII).

It is obvious that the weak acids impart the reversible color change to the complexes, but lewis acids or stronger acids lead to an irreversible color change, such as SB(XVI) and (XVII). When the electron acceptor is phenol, the stronger

the acidity of the phenol is, the deeper the thermochromic degree is (such as SB(I), (IV), (V), and (VII)). It is interesting that the difference between SB(XII) and (XIII) is only solvent compound, but the thermochromic behavior shows greatly distinct, the reason are more accurately approved solvent-stearic acid as proton donor.

On heating, all these complexes except SB(XVI) and (XVII) which give sharp endothermic peaks, gave exothermic peaks and shown the original colors quickly after cooled. We can conclude that these complexes undergo reversible color changes with temperature changing. Also the thermal stability in solid state was established prior or simultaneous to melting.

From the DSC/TG diagram in Fig. 1, we can see four shape and a line, which indicate if the electron acceptors of the complexes are different and also they are dissolved in different solvent, they will undergo different reversible thermochromic process with the temperature variation [9]. Fig. 2 illustrates the mass keep constant in the process. The data of DSC are much more accurate and convictive than that from eye. As for SB(I) and (XII), there were two thermochromic peaks before melting peak, which indicates that twice thermal behavior occurred in the two complexes before melting. As for SB(VII), there was only peak in DSC diagram, that are due to melting and thermal behavior occurred at the same time. As for majority of these complexes such as SB(IX), (X) and (XI), there were a thermochromic peak and a melting peak.

Fig. 2 illustrates the three sorts of reversible thermochromic processes. From Fig. 2, we can perform the classification of these synthesized complexes. SB(I) were ascribed to sort (a), SB(II) and (XII) were ascribed to sort (c), the others were ascribed to sort (b), sort (b) is also the traditional and ordinary reversible thermochromic process.

It can be deduced that there exist a thermal equilibrium between the primary color phase and final one. In order to verify it further, we studied the kinetic properties of the equilibrium and calculated the value of E_a of the color changing peaks of the complexes according to the hypothesis of Maycock [15] and calculating methods of Thomas and Clarke [12]. The equation was showed

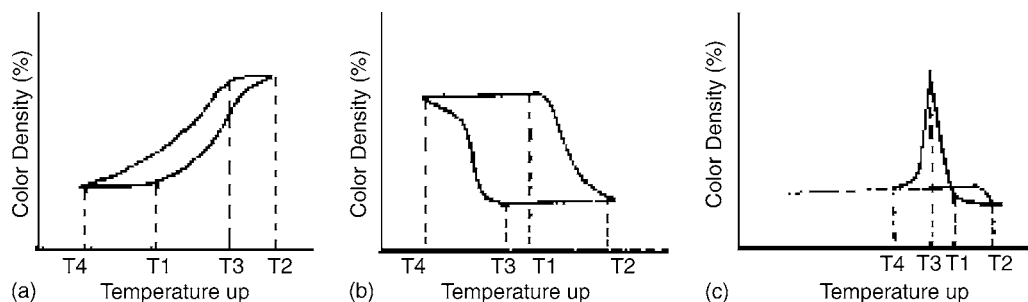


Fig. 2. Curves of three different reversible thermochromic process of the complexes under investigation. T_1 and T_2 are the onset and thermal achromic temperature, respectively; T_3 and T_4 are the returning onset and thermal achromic temperature, respectively.

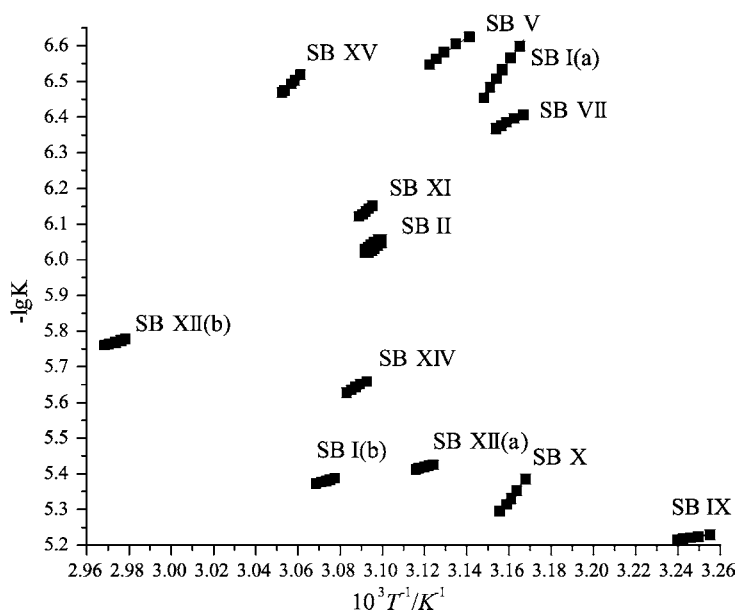


Fig. 3. Kinetic plot of thermochromic process of part of these complexes.

as follows:

$$-\log \left[\frac{(dH/dt)}{A} \right] = \frac{E_a}{2.303RT - \log C}$$

where dH/dt is heat flow, A the peak area, and C the constant.

From Fig. 3, we can see that the points adopted in the range of α from 0.19 to 0.46 have good linear property, and the value of SD, P, and K reached 0.001, 0.0001, and 0.999, respectively. It also proves that the thermochromic process is first-order kinetic process, and the approximate calculating formula is correct and feasible, and the result is true and credible.

It is easy to find that the values of E_a are generally small and have range of 20–90 kJ/mol, while the circumstance can provide the energy range of 30–40 kJ/mol. We can just explain why thermal behavior is easy to occur in these complexes at the room or slightly high temperature. As for SB(II) and (IX), the values of E_a are abnormal high, which can explain that there exists firmer force between electron donor and electron acceptor than others and the solvent begins to partially melt when thermochromism occurs. Also,

we can see the difference from DSC diagrams. So, we can make a conclusion that the stronger the acidic property of electron-acceptor (phenols) is, the deeper the thermochromic color degree is, and the higher the value of E_a is.

Because the complexes are composed of CVL, the electron acceptor and solvent shown good reversible thermochromic behavior, short returning time and high sensitivity in solid state, and they may be used as thermal functional material in many fields. Ring-opened and ring-closed are two stable states, but they can convert to each other through thermalchemical means. With the development of the microcapsuled technique, these new complexes as described in this paper may have more important uses in future functional material.

4. Conclusions

The new 15 complexes were synthesized and characterized. They shown good reversible thermochromic behavior, which undergo a lactone tautomerism mechanism

and the two stably states. Thermochromic color degree and temperature were determined by the acidic properties of electron-acceptor and solvent compounds, respectively. The stronger the acidic property of electron-acceptor is, the deeper the thermochromic color degree is, and the higher the value of E_a is. Thermochromic process of these complexes follows the first-order kinetic equation. From the results obtained, these new complexes provides a potential usage in many fields by means of thermal induced lactone ring tautomerism.

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References

- [1] S.I. Charles, EP 564959 (1993).
- [2] U. Makoto, JP 1173110 (1999).
- [3] Pilot, Inc. Co. Ltd., JP 07258568 (1996).
- [4] H.A. Sergio, N. Alison, et al., *J. Chem. Soc., Perkin. Trans. 2* (1996) 2293.
- [5] T. Masashi, S. Masashi, M. Katsuji, Y. Tadataka, et al., *Dyes Pigm.* 39 (1998) 97.
- [6] D. Aitken, S.W. Burkinshaw, J. Griffiths, A.D. Towns, *Rev. Prog. Color.* 25 (1996) 1.
- [7] F. Katsuyuki, O. Yoshiaki, et al., EP 0873881 (1998).
- [8] G. Hiroshi, JP 0699660 (1994).
- [9] C. Kuniyuki, N. Akio, JP 0920078 (1997).
- [10] T.A. Jacob, WO 9318098 (1993).
- [11] Y. Nianfa, Z. Xingliang, Y. Liwen, *Fine Chem.* 16 (1999) 28.
- [12] J.M. Thomas, T.A. Clarke, *J. Chem. Soc. A* (1968) 457.
- [13] A.W. Mary, L.B. Moinque, *J. Chem. Educ.* 76 (9) (1999) 1201.
- [14] M. Yiping, Z. Beirong, W. Keru, *Pigm. Ind.* 6 (2000) 35.
- [15] J.N. Maycock, *Thermochim. Acta* 1 (1970) 389.