Reversible Coloring/Decoloring Reactions of Thermochromic Leuco Dyes Controlled by a Macrocyclic Compound Developer

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Abstract

In this study, we examine macrocyclic compounds to determine whether they can provide a safer replacement and stable complex for BPA in thermochromic dyes. To achieve this objective, a series of macrocyclic compounds, Methyl-*N*-benzylhexahomo-triazacalix[3]arene (**MeAC3**), *p*-Chloro-*N*-benzylhexahomo-triazacalix[3]arene (**ClAC3**), α -Cyclodextrin (**α -CD**), β -Cyclodextrin (**β -CD**), *p*-tert-Butylthiacalix[4]arene (**TC4**), Calix[4]arene (**C4**) and Resorcin[4]arene (**RC4**) were synthesized. Among these macrocyclic compounds, **RC4** was determined to be the most appropriate candidate to replace BPA as the developer material used in thermochromic dyes. In tests of prepared thermochromic dyes, **RC4** had results similar to those of BPA, achieving the best protonation/deprotonation equilibria and providing a dark contrast with the thermochromic dye. DFT calculations also showed stable complexes between **RC4** and CVL via hydrogen-bond interactions.

1. Introduction

Thermochromic (temperature sensitive) dyes (TC) are materials which change color as a function of temperature [1]. They can be used in several different applications such as sensors, thermal indicators, memory storage devices, security inks, and dyes for solar cells and other luminescent switches of solid-state materials [2–5]. Normally, leuco dye-based TC composites have three components, including a color former (leuco dye), a color developer and a solvent. The color changes in this system result from two competing reactions, one between the dye and the developer and the other between the solvent and the developer. Common color formers, such as spiro lactone, fluoranes, spiropyrans or fulgides, are electron-donating compounds [6]. One of the various types of color formers, crystal violet lactone (CVL), is a classic halochromic dye which has been widely used as a chromogenic reagent in thermochromic systems [7]. Bis-phenol A (BPA) has been intensively used as a color developer because of its efficiency and low cost [8]. However, previous research has shown that BPA exposure can potentially cause various detrimental health effects such as heart disease, breast cancer, infertility, and neuro-developmental disorders [10]. Skin penetration/absorption of BPA for someone simply holding thermal printing papers can reach 71 mg/day [9]. In addition, the absence of stability of a complex system (three components) is also a problem in leuco dye applications. Therefore, many researchers are interested in finding new substrates to serve as suitable color developers. Recently, linear-type and hyperbranched-type polyphenol derivatives have been used as developer materials for temperature sensitive dyes [11, 12]. However, it was found that this type of polymer has a few disadvantages such as poor molecular weight control, high polydispersities, and low blocking efficiencies [13]. The results of these studies have been difficult to interpret, and analysts have reached different conclusions about its use as color developer. Macrocyclic compounds are known as traditional supramolecules based on the specific channel where molecular recognition is possible. Normally, their structure, composed of phenol units and alcohol groups, can be used as a novel developer material. To the best of our knowledge, there have not been any studies about using this type of developer material for temperature sensitive dyes. In this work, we study various

macrocyclic compounds. (**MeAC3**, **CIAC3**, **TC4**, **C4**, α -CD, β -CD and **RC4**) as color developers, as they have good stability, exact molecular weights and good complexation properties.

2. Materials And Methods

2.1. Reagents and Chemicals

All reagents were analytical grade. β -Cyclodextrin was purchased from Acros Organics. α -Cyclodextrin, *p*-chlorophenol, *p*-tert-butylphenol and *p*-cresol were purchased from Fluka. Crystal violet lactone (CVL), 1-octadecanol (OD), resorcinol, formaldehyde 40% w/v and sodium hydroxide (NaOH) were purchased from Carlo Erba Reagents. Hydrochloric acid 37% (HCl) was purchased from Anapure. Tetrahydrofuran (THF, Sigma-Aldrich) was distilled over sodium and benzophenone was distilled under a nitrogen atmosphere. Commercial grade solvents including acetone, hexane, dichloromethane, methanol, and ethyl acetate were distilled before use. Toluene (Labscan) and dimethyl formamide (DMF, Labscan) were dried over CaH_2 and freshly distilled under a nitrogen atmosphere prior to use.

2.2. Instrumentation and Apparatus

^1H -NMR spectra were measured using a Varian 400 MHz spectrometer in CDCl_3 with TMS as an internal reference. Fluorescence spectra in solution were measured with a Perkin Elmer LS 50B spectrometer. Absorbance spectra were recorded with a Perkin Elmer Lambda 25 UV-Vis spectrometer. FT-IR spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer. SEM measurements were performed with a Zeiss (LEO) 1450VP microscope. A Thermogravimetric analysis (TGA) was carried out using a SDT Q600 from TA Instruments.

2.3. Synthesis of *p*-Chloro-*N*-benzylhexahomotriazacalix[3]arene (**CIAC3**)

CIAC3 was synthesized according to a methodology modified from the literature [14]. 4-Chloro-2,6-bis(hydroxymethyl) phenol (6.00 g, 32.52 mmol) and benzylamine (3.39 g, 31.67 mmol) were dissolved in 150 mL of xylene and the resulting mixture was refluxed for 72 h. During the course of the reaction, generated water was removed with a Dean-Stark condenser. The mixture was evaporated to dryness, creating a deep yellow oil. on a silica gel (hexane:EtOAc) 9:1, v/v) (2.73 g, 33% yield) were as follows: ^1H NMR (400 MHz, CDCl_3): δ 7.29 (br s, g 15H, ArH), 7.01 (s, 6H, ArH), 3.69 (s, 6H, NCH_2Ar), 3.64 (s, 12H, NCH_2Ar). FTIR (KBr). ν 3054, 3023, 2832, 2805, 1738, 1602, 1470, 1372, 1240, 1116, 863, 738, 699, 485 cm^{-1} .

2.4. Synthesis of *p*-Methyl-*N*-benzylhexahomotriazacalix[3]arene (**MeAC3**)

Undergoing a process similar to that described for **CIAC3** above, 4-Methyl-2,6-bis(hydroxymethyl)phenol (5.47 g, 32.52 mmol) and benzylamine (3.39 g, 31.67 mmol) was added to 150 mL of xylene. The

resulting mixture was refluxed for 72 h, with generated water removed with a Dean-Stark condenser during the course of the reaction. The mixture was evaporated to dryness, creating a deep yellow oil. The results of chromatography performed on a silica gel (hexane:EtOAc) 9:1, v/v) (3.50 g, 45% yield) were as follows: ^1H NMR (400 MHz, CDCl_3): δ 11.22 (br s, g 3H, OH), 7.22 (br s, g 15H, ArH), 7.03 (s, 6H, ArH), 3.64 (s, 6H, NCH_2Ar), 3.56 (s, 12H, NCH_2Ar), 2.21 (s, 9H, ArCH_3).

2.5. Synthesis of *p*-tert-Butylthiacalix[4]arene (TC4)

TC4 was synthesized in a manner similar to that described in the literature with a slight adjustment [15]. A solution of *p*-tert-butylphenol (64.5 g, 0.43 mol), elemental sulfur S_8 (27.5 g, 0.86 mol), and NaOH (8.86 g, 0.215 mol) in tetraethylene glycol dimethyl ether (19 mL) was stirred under nitrogen. The stirred mixture was gradually heated to 230°C over a period of 4 h and kept at this temperature for a further 3 h with concomitant removal of the evolving hydrogen sulfide by using a slow stream of nitrogen gas. The resulting dark red product was cooled to an ambient temperature and diluted with toluene and ether mixture. Then 0.5 M aq. sulfuric acid was added to the solution using vigorous stirring to get a suspension. The precipitate was collected by filtration, recrystallized with chloroform and dried in vacuo (100°C, 4 hr) to obtain an essentially pure sample of **TC4** (28.53 g, 36.7%). This resulted in ^1H NMR (400 MHz, CDCl_3): δ 9.56 (s, 4H, OH), 7.52 (s, 8H, ArH), and 1.33 (s, 36H, $\text{t-C}_4\text{H}_9$).

2.6. Synthesis of Calix[4]arene (C4)

C4 was synthesized using a process slightly modified from the literature [16]. A solution of *p*-tert-butylphenol (51.81 g, 0.38 mol), 37% formaldehyde solution (34 mL, 0.42 mol) and sodium hydroxide (1.00 g, 0.025 mol) was stirred in an open flask and heated in a silicone bath for *ca.* 2 h at 110-120°C. The reaction mixture was allowed to cool to room temperature and diphenyl ether (900 mL) was then added to the flask. The mixture was transferred to a 1-L one-necked round bottom flask, then the reaction mixture was refluxed under nitrogen for 1.5-2 h until no water vapor remained and cooled to room temperature. Ethyl acetate 300 mL was then added to precipitate the product. After the (*p*-tert-Butylthiacalix[4]arene, **TC4**) precipitate was filtered and dried, it yielded: 28.40 g, 47.1%. ^1H NMR (400 MHz, CDCl_3): δ 10.37s, 4H, ArOH), 7.10 (s, 8H, *m*-ArH), 4.32 (d, J = 14 Hz, 4H_A , ArCH_2Ar), 3.53 (d, J = 13.2 Hz, 4H_B , ArCH_2Ar), and 1.28 (s, 36H, $\text{t-C}_4\text{H}_9$).

Then, a solution of *p*-tert-butylcalix[4]arene, **TC4** (9.88 g, 15.20 mmol), aluminium chloride (9.85 g, 73.80 mmol), phenol (6.95 g, 73.80 mmol) and toluene (50 mL) was stirred under a nitrogen atmosphere at room temperature for 1 h. The reaction mixture was poured into 100 mL of 3 M hydrochloric and stirred for 10 mins, then extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Methanol was subsequently added to precipitate a white powder **C4** (4.23 g, 64.5%), resulting in ^1H NMR (400 MHz, CDCl_3): δ 10.29 (s, 4H, ArOH), 7.12 (d, J = 8 Hz, 8H, *m*-ArH), 6.82 (t, J = 8 Hz, 4H, *p*-ArH), 4.27 (AB, 4H_A , ArCH_2Ar), and 3.54 (AB, 4H_B , ArCH_2Ar).

2.7. Synthesis of resorcin[4]arene (RC4)

A methodology found in the literature was modified to synthesize RC4 [17]. Formaldehyde (4.075 g, 0.1 mol) was immediately added to a solution of resorcinol (14.95 g, 0.1 mol) in H₂O (680 mL) and NaOH (10.86 g, 0.2 mol) at 0°C. The mixture was maintained at 0°C for 2 h with efficient stirring under N₂. After 24 h standing at room temperature, the dark mixture was cooled again to 0°C before being neutralized with HCl (0.2 mol). The brown precipitate that separated from the aq. medium was filtered, washed with H₂O to eliminate HCl and NaCl, and dried. The reddish solid was covered with MeOH (100 mL) and stirred for 2 h to dissolve any impurities. The insoluble material (RC4) was filtrated and dried [3], resulting in ¹H NMR (400 MHz, CDCl₃): δ 9.65 and 9.24 (s, 4H, ArOH), 7.20 and 6.12 (s, 4H, ArH), 4.17 (t, 4H, ArH), 2.20 and 1.28 (8H, CH₂). FTIR (KBr): ν = 3460 cm⁻¹ (-OH), 1430 cm⁻¹ (C-C) and 1280 cm⁻¹ (-CH₂).

2.8. Preparation of leuco dyes (LD1-LD7)

Leuco dyes containing CVL, macrocyclic compounds, and OD were prepared using the following procedure. First, CVL, macrocyclic compounds, and OD in a ratio of 1 (CVL), 6 (macrocyclic compounds) and 100 (OD) were added to a flask with a tight-fitting lid [18]. After the mixture had been heated at 160°C for 30 s, the white 1-octadecanol solid in the prepared samples completely melted into a transparent liquid. The samples returned to their solid forms when cooled to room temperature. The Leuco dye compounds obtained were pale-yellow, white, and blue solids. The macrocyclic compounds used for preparing leuco dyes were composed as follows:

Leuco dye 1 (**LD1**); CVL 0.10 g, 0.24 mmol: **MeAC3** 1.03 g, 1.44 mmol: OD 4.48 g, 24 mmol

Leuco dye 2 (**LD2**); CVL 0.10 g, 0.24 mmol: **CIAC3** 1.12 g, 1.44 mmol: OD 4.48 g, 24 mmol

Leuco dye 3 (**LD3**); CVL 0.10 g, 0.24 mmol: **TC4** 1.04 g, 1.44 mmol: OD 4.48 g, 24 mmol

Leuco dye 4 (**LD4**); CVL 0.10 g, 0.24 mmol: **C4** 0.61 g, 1.44 mmol: OD 4.48 g, 24 mmol

Leuco dye 5 (**LD5**); CVL 0.10 g, 0.24 mmol: **α-CD** 1.47 g, 1.44 mmol: OD 4.48 g, 24 mmol

Leuco dye 6 (**LD6**); CVL 0.10 g, 0.24 mmol: **β-CD** 1.63 g, 1.44 mmol: OD 4.48 g, 24 mmol

Leuco dye 7 (**LD7**); CVL 0.10 g, 0.24 mmol: **RC4** 0.70 g, 1.44 mmol: OD 4.48 g, 24 mmol

2.9. Study of color differences in leuco dyes

Leuco dyes were heated from 30 to 80°C, and color changes were recorded. A larger value of L* (lightness) indicates that the surface of the measured object was light and a smaller value indicates that it was dark. Red-green color changes are represented by a*, with positive values indicating red and negative values signifying green. Yellow-blue color changes are shown by b*, with positive values denoting that the surface of the object measured was yellow, and negative b* values indicating blue. The symbol C* indicates color chroma and h* indicates hue. Thus, color differences were calculated using the following formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Where: ΔL^* (brightness difference) = $L1^* - L2^*$, Δa^* (red and green difference) = $a1^* - a2^*$, and Δb^* (yellow blue difference) = $b1^* - b2^*$. $L1^*$, $a1^*$ and $b1^*$ are all initial values (30°C), while $L2^*$, $a2^*$ and $b2^*$ are the values after the temperature change [19].

3. Results And Discussion

3.1. Macrocyclic compounds

All macrocyclic compounds were prepared using a condensation reaction slightly adapted from the literature [14–17]. The chemical structures of macrocyclic compounds were characterized by ATR-FTIR, $^1\text{H-NMR}$ and mass measurements. As shown in Fig. 1, their structures are typically composed of phenol unit and alcohol groups. These can be used as color developers by acting as proton donors, changing the dye molecule between its leuco and protonated colored forms.

3.2. Leuco dye formation and properties

In order to investigate the color-forming abilities of synthesized macrocyclic compounds, mixtures of macrocyclic compounds CVL and OD in a ratio 1 (CVL) : 6 (macrocyclic compounds) : 100 (OD) were prepared. The mixture was then heated on a hot plate at 160°C for 30 s until completely melted (molten mixture). All samples were brought back to solid form by cooling them to room temperature. Fig. 2 shows photographs of the leuco dyes **LD1-LD7** before and after heat treatment. It was found that only **LD7** exhibited a blue to black color change when taken from room temperature to 160°C. A color change in **LD7** upon heating (160°C) indicated that in the presence of **RC4**, CVL dyes underwent a structural change. They transformed from a closed-lactone form to an open-lactone form when heated due to the release of protons from developer materials, and thus turned black [11]. In addition, this colored/decolored reaction was reversible for more than several cycles. On the other hand, no CVL chemical, structural or color changes occurred in other leuco dyes (**LD1-LD6**).

The opening of lactone rings in CVL dyes in **LD7** was confirmed using ATR-FTIR measurements. The spectra of **LD7** and pure compounds are shown in Fig. 3. Pure CVL exhibited C-C stretching in the aromatic ring at 1611 and 1440 cm^{-1} . A strong peak appearing at 1070 cm^{-1} was attributed to C-O stretching. The O-H stretching of **RC4** appeared at 3316 cm^{-1} . Peaks at 2933 and 2859 cm^{-1} belonged to the $-\text{CH}_2$ asymmetric stretching vibration of an aliphatic chain. In the spectra of **LD7**, a sharp lactone stretching band (C=O) near 1740 cm^{-1} of **LD7** clearly decreased and slightly shifted to 1755 cm^{-1} after heating because of a ring opening caused by protonation of the lactone structure of CVL dyes [20]. The color-forming reaction tests in **LD7** confirms that **RC4** is capable of complexation forming and opening the lactone ring of Leuco dyes by releasing protons from phenolic groups.

Additionally, the thermal stability of macrocyclic compounds and leuco dyes (**LD1-LD7**) were studied using the TGA method. The TGA thermogram in Fig. 4a shows that the initial temperature causing a 10%

weight loss in all macrocyclic compounds was above 250°C. In the cases of **CIAC3** and **RC4**, the TGA indicates that under normal atmospheric conditions, the macrocyclic compounds transformed into thermal-resistant residuals such as polymer [21]. Fig. 4b shows that **LD1-LD7** had a 10% loss weight at 240°C, and just 20% of the original sample weight remained at 800°C. A TGA curve of **LD7** shows an increasing in percentage of weight loss (in which %residue decreased from 42–19%) which might be explained by complexation between **RC4** and CVL leading to a decrease in thermal-resistant residual species.

The morphology and particle size distribution of the microcapsules were determined by means of SEM photographs. Fig. 5 shows the microstructure of leuco dye pigments using BPA and **RC4** as color developers. Fig. 5a and 5b are SEM images of leuco pigments which have average diameters of 0.3-0.6 μm and were developed with BPA. Fig. 5c and 5d are SEM images of leuco pigments which have average diameters of 2.8-3.5 μm and were developed with **RC4**. The SEM micrograph of **RC4** shows an increase in crystallinity and particle size when compared to conventional BPA developers. These results might be attributed to π - π interactions and hydrogen bonding of **RC4** and CVL in leuco dyes [22].

3.3. Computational study

To further study the properties of CVL, **RC4** and **LD7**, optimized geometries and HOMO and LUMO energies were computed using density functional theory (DFT) calculations at a B3LYP/LanL2DZ theoretical level through the Gaussian 09 program [23]. The lowest energy structures of CVL **RC4** and **LD7** are shown in Fig. 6. It is clearly seen that the molecular geometries of CVL and **RC4** found in **LD7** distorted from their free forms and intermolecular hydrogen bonds ($\text{OH}\cdots\text{O}$) appeared in the complex. The $\text{OH}\cdots\text{O}$ hydrogen bond distance was found to be 1.78 Å. In addition, the calculated energies of **LD7** (-3005.7 a.u.) were lower than those of both CVL (-1322.7 a.u.) and **RC4** (-1683.0 a.u.). As demonstrated in the optimized structures, it was found that **RC4** could form stable complexes with CVL using complexation, as shown in Fig. 6.

The electron distributions and orbital energies of the HOMO and LUMO of CVL (lactone form), and **RC4** and **LD7** (OD, **RC4**, CVL^+ (cationic form)) are presented in Fig. 7. In the cases of CVL and CVL^+ , the HOMO were all localized on a phenyl unit. However, the LUMO were localized on lactone units in CVL and uniformly distributed throughout the entire molecule in CVL^+ , suggesting that cationic forms are more extensively delocalized than lactone forms. Furthermore, both HOMO and LUMO of **RC4** and CVL^+ in **LD7** are different from those of free molecules. The HOMO levels of CVL, **RC4** and **LD7** have energy values of -0.181, -0.206, and -0.182 eV, respectively. The LUMO levels of CVL, **RC4** and **LD7** have energy values of -0.040, -0.026, and -0.061 eV, respectively. The results indicate that the energy band gap of **LD7** (0.121 eV) is considerably smaller than that of CVL (0.141 eV) and **RC4** (0.180 eV), and the cationic form in **LD7** is more delocalized than the lactone form in CVL owing to the hydrogen-bond interactions of the color former-developer [24].

3.4. Color differences in Leuco dyes

Digital photography was used to evaluate the effect of temperature changes on color. The methodology used a bulk molten mixture of **LD7** in vials, tempered in a water bath. After reaching desired temperature, the samples were removed from the water bath and an image was recorded using a digital camera. Then, images were transformed into trichromatic values XYZ, with consequent calculations of visual color differences. The trend of **LD7** color difference variations based on temperature changes from 30-80°C is shown in Fig. 8. The color of **LD7** changed from blue to black as the temperature increased. When the molten mixture of **LD7** was heated to 60°C, the color changed significantly. The color of **LD7** began to change around 60°C.

4. Conclusion

We report on a series of macrocyclic compounds (**MeAC3**, **CIAC3**, **TC4**, **C4**, α -**CD**, β -**CD** and **RC4**) which were prepared to investigate their feasibility as developer materials for temperature sensitive dyes. After analyzing various macrocyclics, **RC4** is found to be the most appropriate candidate for a novel color developer in temperature sensitive dye thermal papers based on its coloring/decoring reactions. It is found that **RC4** has a high static sensitivity and a dark contrast of leuco dye, similar to that found in BPA. This first successful demonstration of the use of macrocyclic compounds as developer materials for temperature sensitive dyes opens up a new pathway for the development of macrocyclic compounds as replacements for problematic BPA developer materials.

Declarations

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Availability of data and material Not applicable (All data generated or analyzed during this study are included in this published article).

Code availability Not applicable.

Authors' contributions S. Sriphalang, C. Kaewtong and D. Pattavarakorn contributed to the study conception and design. The DFT calculations were performed by S. Sriphalang and B. Wanno. The experimental procedures were performed by S. Sriphalang, A. Saenkham, T. Chaodongbung, C. Kaewtong and D. Pattavarakorn. The data analysis and the first draft of the manuscript were made by C. Kaewtong, D. Pattavarakorn, and B. Wanno. Revising the manuscript critically for important intellectual content on

subsequent versions of the manuscript has done by S. Sriphalang, A. Saenkham, T. Chaodongbung, C. Kaewtong and D. Pattavarakorn All the authors read and approved the final manuscript.

Declarations The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

p-Methyl-*N*-benzylhexahomotriazacalix[3]arene (**MeAC3**)

p-Chloro-*N*-benzylhexahomotriazacalix[3]arene (**ClAC3**)

α -Cyclodextrin (**α -CD**)

β -Cyclodextrin (**β -CD**)

p-tert-Butylthiacalix[4]arene (**TC4**)

Calix[4]arene (**C4**)

Resorcin[4]arene (**RC4**)

Figure 1

Structure of macrocyclic compounds synthesized via a condensation reaction.

Figure 2

Photographs of **LD1-LD7** before (up) and after (down) heat treatment at 160°C for 30 s.

Figure 3

ATR-FTIR spectra of CVL, **RC4** and **LD7**.

a)

b)

Figure 4

TGA curves of macrocyclic compounds (a) and **LD1-LD7** (b).

a)

b)

Figure 5

SEM: 500x(a), 10,000x(b), leuco pigments with average diameters of 0.3-0.6 μm that were developed with BPA. 500x(c), 10,000x(d) and leuco pigments with average diameters of 2.8-3.5 μm that were developed with **RC4**.

Figure 6

The optimized structures of **CVL**, **RC4** and **LD7**, obtained at a B3LYP/LanL2DZ level of theory with the lowest energy structures in a.u..

Figure 7

Molecular orbital diagrams and calculated HOMO-LUMO energy levels of **CVL**, **RC4** and **LD7**.

Figure 8

Photographs of **LD7** at various temperatures (30-80°C) (up) and graph of color differences in **LD7** as a result of heating and cooling processes (down).

Supplementary Files

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