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Thermochromic and solvatochromic zinc biladienones: dynamic equilibria of a metal complex having a flexible framework sensitive to environment

Kojiro Kita,[a] Taiyo Tokuoka,[a] Eriko Monno,[a] Shigeyuki Yagi,[b] Hiroyuki Nakazumi[b] and Tadashi Mizutani[a,*]

[a]*Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan*
[b]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 599-8531, Japan*

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Abstract—Dehydration of zinc biladienone was catalyzed by zinc acetate, while the reverse reaction was catalyzed by triethylamine. The transformation can be performed thermally without catalyst, and the ratio of the hydrated form to the dehydrated form depended on the solvents: the dehydrated form is favored in $CHCl_3$ and CH_2Cl_2, while the hydrated form is favored in hexane, pyridine, and DMF. Kinetic studies on the thermal transformation of zinc biladienone from its hydrated blue form to the dehydrated yellow-brown form were performed in toluene and THF. The rate law was half order with respect to the zinc biladienone concentration in toluene, while first order in THF, leading to a slow transformation in concentrated solution in toluene.

Linear tetrapyrroles such as phytochromobilin and phycocyanobilin function as a prosthetic group in a photoreceptor protein, converting the photon signal to conformational changes in the protein.[1] The flexible framework and several hydrogen bonding sites endow the molecules with the unique properties. We have been interested in the flexible framework of linear tetrapyrroles, particularly its metal complex, focusing on the application of metallobilindiones to chirality sensors and signal transduction systems, by taking advantage of the flexible chiral framework of bilindiones.[2]

Acylbiladienones having an acyl group at the terminal pyrrole were isolated as one of the catabolites of chlorophyll,[3] and they are also obtained by the oxidation of porphyrins.[4] Recently we reported that coupled oxidation of the iron complex of tetraarylporphyrins gave benzoylbiladienones in a good yield.[5] Some metal complexes of linear tetrapyrroles show coordination isomerism, another interesting feature as a functional pigment. Smith et al.[6] revealed that the nickel complex of biladienone has two coordination isomers, the 4N complex with four nitrogens coordinated and the 3N+O complex with three nitrogens and one oxygen coordinated.

Hewlins and co-workers reported that the zinc complex of triphenylbenzoylbiladienone exists either as a blue complex (**1b**) or a dehydrated yellow-brown complex (**2b**).[7] They found that the initial product of the reaction of biladienone with zinc acetate is **1b**. Upon heating **1b** was transformed into **2b**, which was gradually transformed into **1b** when left in chloroform. During our investigation of the thermal properties of zinc biladienones bearing long alkyl chains to develop functional materials, we found that a solution of **2b** in chloroform was stable, and was not transformed into **1b** contrary to previous report. The equilibrium between the blue complex and the yellow-brown complex was more complicated than was originally described. We report here novel findings that the dehydration equilibrium is governed by a number of factors such as solute–solvent interactions involving the coordination of solvent to the zinc, interactions of the zinc complex with Lewis acid or Lewis base, the water concentration in solutions, and the aggregation equilibrium of the blue complex.

Keywords: Biladiene; Bilin; Zinc; Solvatochromism; Thermochromism.

* Corresponding author. Tel.: +81 774 65 6623; fax: +81 774 65 6794; e-mail: tmizutan@mail.doshisha.ac.jp

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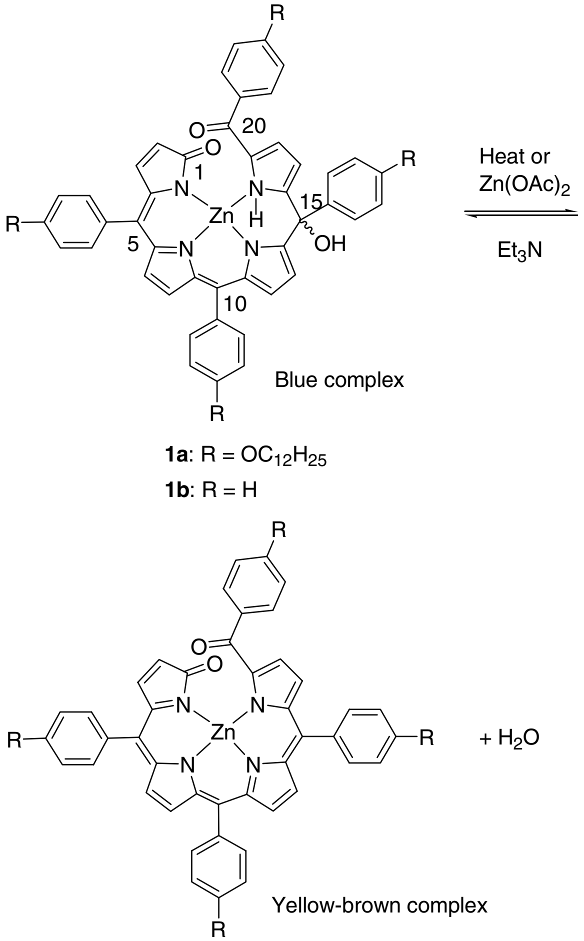
The reaction of zinc biladienone with acid and base found in this study can be used to prepare the blue complex and the yellow-brown complex.



1a: R = $OC_{12}H_{25}$
1b: R = H

2a: R = $OC_{12}H_{25}$
2b: R = H

20-Benzoyl-1,21-dihydro-15-hydroxy-5,10,15-triphenylbiladien-1-one-*ab* with and without *para*-dodecyloxy groups were prepared by the coupled oxidation of the iron complexes of tetra(*p*-dodecyloxyphenyl)porphyrin and tetraphenylporphyrin, respectively.[5,8] The free base biladienones were fully characterized by ^{1}H NMR, COSY, ROESY, HMBC, and FAB-MS.[9] The free base biladienones in chloroform were treated with a methanolic solution of zinc acetate to obtain the zinc complexes. The progress of the reaction was monitored by UV–vis spectroscopy. A blue complex **1a** showing the absorption maxima at 584 and 630 nm in CH_2Cl_2 was immediately formed, and it was gradually transformed into the yellow-brown complex **2a** showing the absorption maximum at 477 nm in CH_2Cl_2. After a usual work-up, evaporation of the solvent and washing the chloroform solution with water, **2a** was isolated. When the isolated neat **2a** was left at room temperature in air, it gradually transformed into **1a**. ^{1}H NMR of **2a** in $CDCl_3$ showed eight doublets of β-pyrrole protons and eight doublets of phenylene groups. These resonances were assigned using COSY, ROESY, and HMBC spectra.[10] ^{1}H NMR of **1a** in $CDCl_3$ was rather complex, and full assignment of the resonances was not performed.[11]

A solution of **1a** was transformed into **2a** upon heating to 80–100 °C. The transformation also proceeds slowly at room temperature, and the equilibrium mixture contains both **1a** and **2a** in a ratio, which is determined by the solvent. After 3 days at 25 °C, the ratios of **1a** to **2a** determined by UV–vis spectra were 0:100 ($CHCl_3$), 3:97 (CH_2Cl_2), 10:90 (EtOAc), 47:53 (toluene), 58:42 (THF), 85:15 (hexane), 93:7 (pyridine), and 99:1 (DMF). For zinc biladienone without long alkyl groups, **1b** is predominant in THF and ethyl acetate, while **2b** is predominant in chloroform and dichloromethane. The equilibrium between **1a** and **2a** depends on the concentration of water in solutions. In the presence of 0.185 M of water in toluene, dichloromethane, THF, or EtOAc, the equilibrium was shifted toward **1a**. After 3 days at 25 °C, the ratios of **1a** to **2a** in the presence of 0.185 M water were 33:67 (CH_2Cl_2), 55:45 (EtOAc), 78:22 (toluene), and 88:12 (THF).

The transformation from **1a** to **2a** was also catalyzed by the addition of zinc acetate, and the reaction proceeded smoothly at room temperature (see Fig. 1). The reaction can be catalyzed by the coordination of the Lewis acidic zinc to the hydroxyl group. The addition of triethylamine to a CH_2Cl_2 solution of **2a** caused the transformation to **1a**. In a solution of 8.1×10^{-6} M of **2a** and 2.4×10^{-4} M of triethylamine in CH_2Cl_2, decrease in the absorbance at 481 nm due to **2a** was monitored at 25 °C to give the first-order rate constant to be 2.03 s^{-1}. In the absence of triethylamine, no transformation to **1a** was observed.

Temperature change caused the shift of the equilibrium as described above. The rate of the transformation from **1a** to **2a** was accelerated at higher temperature. The ratio of the initial rate at 50 °C to that at 40 °C was 4.5–5.8. Interestingly, in toluene, the rate of transformation was concentration dependent, the conversion to **2a**

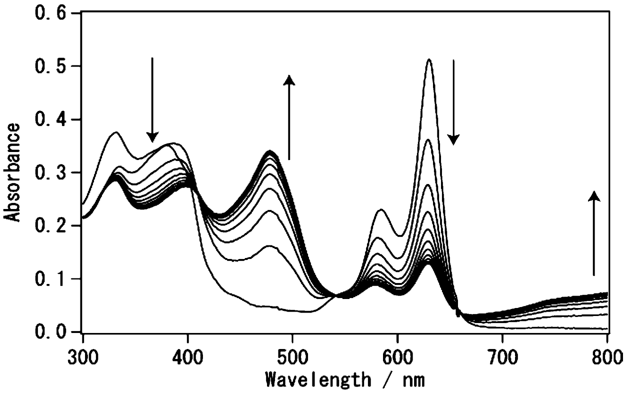


Figure 1. UV–vis spectral changes of **1a** in CH_2Cl_2 upon addition of $Zn(OAc)_2$. To 3 mL of 8.1×10^{-6} M of **1a** was added 0.1 mL of 5.5×10^{-2} M of $Zn(OAc)_2$ in methanol. Spectra were recorded every 20 min at 25 °C. $t_{1/2} = 26$ min.

was faster in a dilute solution than in a concentrated solution. In order to clarify this peculiar behavior, we determined the order of the rate by the initial rate method (Fig. 2). The rate is proportional to the half order in **1a** in toluene,[12] while it is proportional to the first order in **1a** in THF.

$$-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = k_{\mathrm{app}}\sqrt{[\mathbf{1a}]} \text{ in toluene,}$$

$$-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = k[\mathbf{1a}] \text{ in THF.}$$

The apparent rate constant in toluene, k_{app}, was determined using the following equation:

$$\sqrt{[\mathbf{1a}]} - \sqrt{[\mathbf{1a}]_0} = -\frac{1}{2}k_{\mathrm{app}}t,$$

where $[\mathbf{1a}]_0$ is the initial concentration of **1a**.

The rate constants determined in the concentration range of **1a** of 6×10^{-6} to 3×10^{-5} M was constant, indicating the validity of the rate equation. In THF, the rate followed the simple first-order kinetics, and the rate constant was obtained by assuming the following equation: $\ln [\mathbf{1a}]/[\mathbf{1a}]_0 = kt$. In a mixed solvent, toluene/THF = 95:5 (vol/vol), the rate was faster than in toluene but it followed the half-order kinetics: $k_{\mathrm{app}} = (1.24 \pm 0.08) \times 10^{-6}\ \mathrm{M}^{1/2}\,\mathrm{s}^{-1}$ at 50 °C. The rate constants in toluene and THF are listed in Table 1.

The half-order kinetics have been observed when the pre-equilibrium from a dimer to a monomer is involved in the reaction pathway.[12] In the present case, the following reaction pathway can account for the half-order kinetics (Scheme 1). The blue complex exists either as a dimer or as a monomer, and the equilibrium constant of the dimer dissociation is K. We assume that only monomeric **1a** will give **2a** with the first-order rate constant k_1.

Then the rate equation is expressed by

$$-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = k_1[\mathbf{1a}] \qquad (1)$$

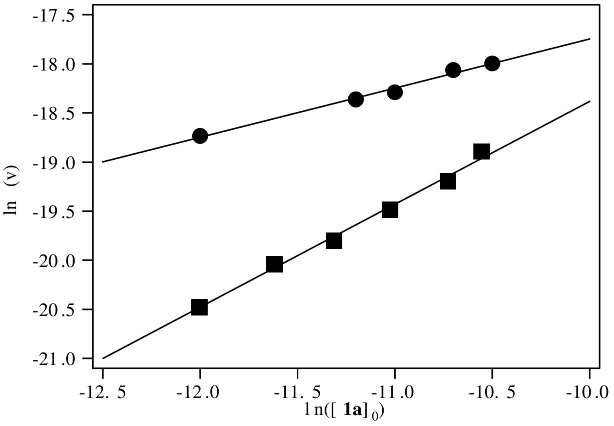


Figure 2. Log–log plot of the initial rate, v, and the concentration of the blue complex $[\mathbf{1a}]_0$. ●: in toluene at 60 °C, the equation of the regression line is $(-12.7 \pm 0.3) + (0.50 \pm 0.03)x$; $R^2 = 0.99$, ■: in THF at 50 °C, the equation of the regression line is $(-7.9 \pm 0.5) + (1.05 \pm 0.04)x$; $R^2 = 1.00$.

Table 1. The rate of transformation of **1a** to **2a**

Solvent	T (°C)	Order, n	k_{app}
Toluene	40	0.5	1.96×10^{-7} [a]
	50	0.5	7.21×10^{-7} [a]
	60	0.5	2.78×10^{-6} [a]
THF	40	1	8.03×10^{-5} [b]
	50	1	2.09×10^{-4} [b]
	60	1	5.87×10^{-4} [b]

[a] $\mathrm{M}^{1/2}\,\mathrm{s}^{-1}$.

[b] s^{-1}.

$$(\mathbf{1a})_2 \xrightleftharpoons{K} 2\ \mathbf{1a}$$

$$\mathbf{1a} \xrightarrow{k_1} \mathbf{2a}$$

Scheme 1. Transformation from **1a** to **2a** in toluene.

and the equilibrium constant is given by

$$K = \frac{[\mathbf{1a}]^2}{[(\mathbf{1a})_2]}$$

In the UV–vis spectrum, we cannot discriminate the dimer from the monomer, and the rate of the decrease in the total concentration, $[\mathbf{1a}]_{\mathrm{T}}$, was determined.

$$[\mathbf{1a}]_{\mathrm{T}} = [\mathbf{1a}] + 2[(\mathbf{1a})_2]$$

We also assume that the dimer is favored in the equilibrium: $[\mathbf{1a}] \ll [(\mathbf{1a})_2]$, then

$$K = \frac{[\mathbf{1a}]^2}{[\mathbf{1a}]_{\mathrm{T}}/2}$$

$$\therefore\quad [\mathbf{1a}] = \sqrt{\frac{K}{2}[\mathbf{1a}]_{\mathrm{T}}}$$

Therefore, Eq. 1 leads to

$$-\frac{\mathrm{d}[\mathbf{1a}]_{\mathrm{T}}}{\mathrm{d}t} = k_1\sqrt{\frac{K}{2}}\sqrt{[\mathbf{1a}]_{\mathrm{T}}}$$

This equation explains the half-order kinetics with respect to the concentration of the blue complex. According to this scheme, the apparent rate constant, k_{app}, is equal to $k_1(K/2)^{1/2}$.

The Eyring plot of $\ln(k_{\mathrm{app}}/T)$ against T^{-1} gave the activation enthalpy and the activation entropy of transformation from **1a** to **2a** in toluene to be 112 kJ/mol and −13.8 J/mol/K, respectively. In THF, the activation enthalpy and the activation entropy were 83.5 kJ/mol and −57.2 J/mol/K, respectively. According to the above mechanism, the activation enthalpy and the activation entropy in toluene involve the dissociation to a monomer, and such process should be associated with a positive enthalpy change and a positive entropy change. Therefore, the larger activation enthalpy and the larger activation entropy in toluene are consistent with the proposed reaction scheme.

^{1}H NMR and fluorescence studies also corroborated the aggregation of the blue complex in nonpolar solvents. ^{1}H

NMR of the blue complex exhibited 16 resonances owing to the β-protons of pyrroles in toluene and $CDCl_3$, while only 8 resonances in MeOH-d_4, pyridine-d_5, and DMSO-d_6. In THF-d_8, broad resonances were observed, indicating that there are chemical exchanges between different species. The blue complex **1a** fluoresces in polar solvents such as acetone, MeOH, and DMF, while it does not fluoresce in toluene, benzene, and cyclohexane. On the other hand, **2a** did not fluoresce both in polar and nonpolar solvents.

In conclusion, we showed that the blue zinc biladienone was transformed into the yellow-brown zinc biladienone chemically by the use of $Zn(OAc)_2$ and the reverse transformation was driven by the use of Et_3N. The rate of thermal transformation of the blue complex to the yellow-brown complex was slower in a concentrated solution in toluene. The kinetics can be ascribed to the dissociation of a dimer to a monomer before the dehydration reaction.

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9. Free base of **1a**: ^{1}H NMR ($CDCl_3$) δ 12.31 (br s, 1H), 11.01 (br s, 1H), 9.90 (br s, 1H),7.89 (d, $J = 9.2$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 9.2$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 6.92–6.97 (m, 6H), 6.89 (d, $J = 5.4$ Hz, 1H), 6.86 (d, $J = 9.2$ Hz, 2H), 6.81–6.83 (m, 2H), 6.52 (d, $J = 4.6$ Hz, 1H), 6.38 (d, $J = 8.4$ Hz, 1H), 6.31 (s, 1H), 6.15–6.18 (m, 3H), 3.99–4.04 (m, 6H), 3.93 (t, $J = 6.9$ Hz, 2H) 1.75–1.82 (m, 8H), 1.27–1.50 (m, 72H), 0.86–0.89 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 183.37, 173.30, 164.55, 162.28, 160.79, 159.35, 159.28, 150.19, 149.51, 143.09, 142.24, 139.07, 137.70, 135.64, 134.39, 133.40, 132.20, 132.05, 131.09, 130.96, 130.44, 129.57, 128.46, 125.74, 125.19, 123.96, 121.34, 118.90, 114.38, 114.06, 113.83, 111.67, 109.58, 74.73, 68.27, 68.25, 68.20, 31.93, 29.36–29.68, 26.04–26.12, 22.70, 14.11; FAB MS *m*/*z* 1385 ($[M-OH^-]$); UV–vis (CH_2Cl_2, 25 °C) $\varepsilon_{321} = 43{,}400$, $\varepsilon_{381} = 30{,}500$, $\varepsilon_{569} = 25{,}200\ M^{-1}\ cm^{-1}$.
10. ^{1}H NMR of **2a** ($CDCl_3$): δ 0.89 (m, 12H), 1.2–1.55 (m, 80H), 1.83 (m, 8H), 4.01 (m, 8H), 5.60 (1H, d, $J = 5.4$ Hz, H-2), 6.56 (1H, d, $J = 4.6$ Hz, H-8), 6.62 (1H, d, $J =$ 3.9Hz, H-17), 6.67 (1H, d, $J = 5.4$ Hz, H-3), 6.78 (1H, d, $J = 3.9$ Hz, H-18), 6.87 (2H, d, $J = 9.2$ Hz, H-3′ of 20-phenyl), 6.90 (1H, d, $J = 5.4$ Hz, H-7), 6.95 (4H, d, $J = 8.4$ Hz, H-3′ of 5- and 10-phenyl), 6.97 (1H, d, $J = 4.6$ Hz, H-13), 7.03 (2H, d, $J = 8.4$ Hz, H-3′ of 15-phenyl), 7.16 (1H, d, $J = 4.6$ Hz, H-12), 7.35 (4H, br d, $J = 7.7$ Hz, H-2′ of 5- and 10-phenyl), 7.96 (2H, d, $J = 9.2$ Hz, H-2′ of 20-phenyl). Selected signals of ^{13}C NMR of **2a**: δ 68.0–68.2 (α-C of O), 168.0 (C-6, coupled with a signal at 6.56 ppm in ^{1}H NMR), 182.2 (C-1, coupled with a signal at 5.6 ppm in ^{1}H NMR), 186.1 (C-20, coupled with a signal at 7.96 ppm in ^{1}H NMR). FAB MS *m*/*z* 1448 ($[M+H^+]$); UV–vis (CH_2Cl_2, 25 °C) $\varepsilon_{330} = 31{,}800$, $\varepsilon_{405} = 31{,}000$, $\varepsilon_{480} = 49{,}000$, $\varepsilon_{575} = 7480$, $\varepsilon_{628} = 6090$, $\varepsilon_{750} = 8620$, $\varepsilon_{820} = 10{,}900\ M^{-1}\ cm^{-1}$.
11. ^{1}H NMR of **1a** (toluene-d_8): δ 0.92 (m, 12H), 1.2–1.5 (m, 72H), 1.5–1.75 (m, 8H), 3.55–3.7 (m, 8H), 5.62 (d, $J = 4.6$ Hz, 0.5H), 6.13 (t, $J = 4.5$ Hz, 0.5H), 6.32 (t, $J = 4.5$ Hz, 0.5H), 6.35 (t, $J = 3.8$ Hz, 0.5H), 6.43 (t, $J = 4.5$Hz, 0.5H), 6.45 (d, $J = 4.5$ Hz, 0.5 H), 6.52 (m, 1H), 6.60 (d, $J = 8.4$ Hz, 2H), 6.68–6.82 (m), 6.84–6.90 (m), 7.27 (m, 2H), 7.45 (d, $J = 9.2$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.99 (s, 0.5H), 8.04 (s, 0.5H), 11.61 (s, 0.5H), 13.67 (s, 0.5H). FAB MS *m*/*z* 1448 ($[M-OH^-]$); UV–vis (CH_2Cl_2, 25 °C) $\varepsilon_{332} = 44{,}600$, $\varepsilon_{380} = 42{,}800$, $\varepsilon_{584} = 27{,}800$, $\varepsilon_{630} = 64{,}100\ M^{-1}\ cm^{-1}$.
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