Chlorophyll- and Bacteriochlorophyll-Derived Colorimetric Chemosensors for Amine Detection

Shin-ichi Sasaki,[1,2] **Yuki Kotegawa,**[1] **and Hitoshi Tamiaki***[1]

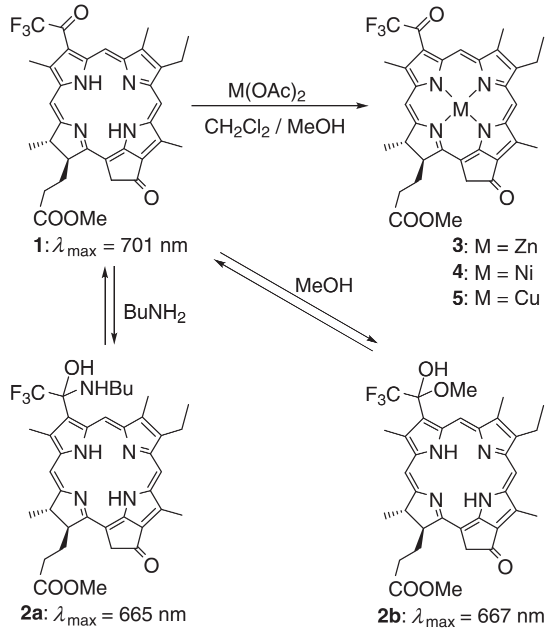
[1]Department of Bioscience and Biotechnology, Faculty of Science and Engineering,
Ritsumeikan University, Kusatsu 525-8577

[2]Nagahama Institute of Bio-Science and Technology, Nagahama 526-0829

Received September 16, 2008; E-mail: tamiaki@se.ritsumei.ac.jp

Chlorophyll and bacteriochlorophyll derivatives possessing a trifluoroacetyl group at the 3-position were synthesized as new colorimetric sensors for amine detection. α-Amino alcohol formation of the free-base chlorin and metallochlorins showed visual color changes from brown to purple and from green to blue, respectively. On the other hand, bacteriochlorin derivative showed large blue-shifts of the Q_y peak in the near-infrared region (775 → 724 nm) and the Q_x peak in the visible region (549 → 520 nm), which are advantageous points for amine sensing. Clear color change was observed from pink to turquoise by the formation of α-amino alcohol adduct.

Development of artificial chromo/fluororeceptors for the selective recognition of biologically important species has attracted much attention because of their possible application to chemical sensors such as optodes.[1] Many functional dyes having various binding sites for target molecules have been designed and synthesized to date.[2,3] One of the unique binding units is the trifluoroacetyl group on an aromatic ring. Although trifluoroacetophenone derivatives have been exclusively used as ionophores for carbonate-selective electrodes,[4,5] recent reports include applications as sensing components toward alcohols,[6] amines,[7] anions,[8] and amino acids.[9] The functional group can reversibly form adducts with those analytes, and stilbene,[6a] azobenzene,[7] pyrene,[9b] and dansyl units[8b,10] have been used as chromo/fluorogenic dye moieties. We recently reported the synthesis of trifluoroacetylchlorin as the first example of a chemosensor using a chlorophyll derivative as a main dye unit.[11] The functionalized chlorin showed a blue shift of the Q_y peak from 701 to 665 nm due to the α-amino alcohol formation (**1** → **2a** in Scheme 1), accompanied by a visible color change from brown to purple. To realize other types of color changes and/or amine detection at a longer wavelength region, here we examined the characteristics of metallated and metal-free trifluoroacetylchlorins as well as metal-free trifluoroacetylbacteriochlorin.



Scheme 1. α-Amino alcohol and hemiacetal formation of trifluoroacetylchlorin **1** to **2a** and **2b**, and preparation of its metal complexes **3**–**5**.

Experimental

General. Proton peaks were assigned by ^1H–^1H COSY and NOESY spectra, and carbon peaks except for quaternary peaks by DEPT and ^{13}C–^1H COSY spectra. Methyl 3-deacetyl-3-formyl-bacteriopyropheophorbide-*a* (**6**) was prepared as previously reported.[12] THF was distilled over CaH_2 before use. Other solvents and reagents were employed as purchased without further purification. All synthetic procedures were done in the dark.

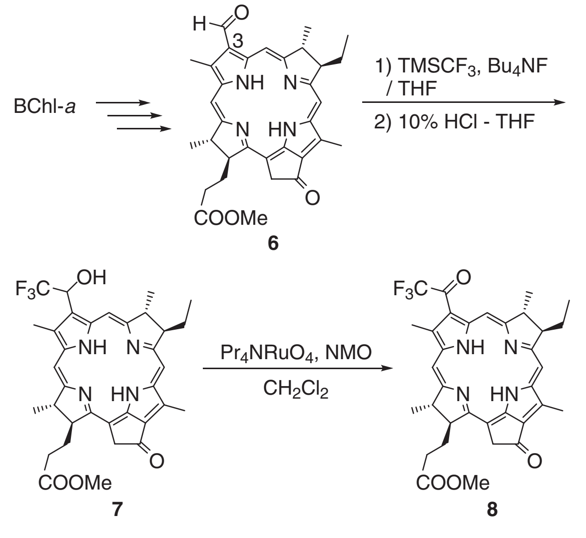
Zinc–Chlorin 3, Nickel–Chlorin 4, and Copper–Chlorin 5. Metal insertion to free-base chlorin **1** were performed by a standard procedure.[13] **3**: Mp 160–162 °C; vis (toluene) λ_{max} 689 (ε/M^{-1} cm^{-1}, 46000), 437 (42000), 379 nm (33000); ^1H NMR (1% pyridine-d_5/CDCl$_3$, 600 MHz): δ 9.81 (1H, s, 5-H), 9.64 (1H, s, 10-H), 8.65 (1H, s, 20-H), 5.24, 5.13 (each 1H, d, $J = 19$ Hz, 13^1-CH$_2$), 4.49 (1H, dq, $J = 2$, 7 Hz, 18-H), 4.28 (1H, dt, $J = 8$, 2 Hz, 17-H), 3.78 (2H, q, $J = 8$ Hz, 8-CH$_2$), 3.71 (3H, s, 12-CH$_3$), 3.62 (3H, s, 2-CH$_3$), 3.58 (3H, s, COOCH$_3$), 3.29 (3H, s, 7-CH$_3$), 2.60, 2.26 (each 1H, m, 17-CH$_2$), 2.44, 2.01 (each 1H, m, 17^1-CH$_2$), 1.75 (3H, d, $J = 7$ Hz, 18-CH$_3$), 1.71 (3H, t, $J = 8$ Hz, 8^1-CH$_3$); ^{13}C NMR (1% pyridine-d_5/CDCl$_3$, 150 MHz): δ 196.9 (C13^1), 183.0 (q, $^2J_{C-F} = 36$ Hz, C3^1), 173.3, 166.0, 161.2, 158.0, 150.6, 149.9, 149.1, 147.7, 144.2, 143.5, 142.3, 136.5, 135.9,

Published on the web February 13, 2009; doi:10.1246/bcsj.82.267

133.5, 130.6 (C1, 2, 3, 4, 6, 7, 8, 9, 11, 12, 13, 14, 16, 17^3, 19), 116.9 (q, $^1J_{\mathrm{C–F}} = 289$ Hz, C3^2), 105.6 (C15), 105.0 (C10), 102.2 (C5), 93.5 (C20), 51.6 (C17^5), 51.2 (C17), 48.5 (C13^2), 48.2 (C18), 30.3 (C17^1), 29.7 (C17^2), 23.7 (C18^1), 19.5 (C8^1), 17.4 (C8^2), 13.3 (q, $^5J_{\mathrm{C–F}} = 3$ Hz, C2^1), 12.9 (C12^1), 11.0 (C7^1); ^{19}F NMR (1% pyridine-d_5/CDCl$_3$, 564 MHz): δ −73.90 (s, 3^1-CF$_3$); MS (TOF) m/z 680 (M$^+$). **4**: Mp 268–269 °C; vis (toluene) $\lambda_{\max}$ 685 (relative intensity, 100%), 421 (79), 380 nm (70); ^{1}H NMR (CDCl$_3$, 600 MHz): δ 9.65 (1H, s, 5-H), 9.41 (1H, s, 10-H), 8.43 (1H, s, 20-H), 4.84, 4.94 (each 1H, d, $J = 20$ Hz, 13^1-CH$_2$), 4.36 (1H, q, $J = 7$ Hz, 18-H), 4.08 (1H, m, 17-H), 3.63 (1H, m, 8- CH$_2$), 3.61 (3H, s, COOCH$_3$), 3.52 (3H, s, 12-CH$_3$), 3.44 (3H, s, 2-CH$_3$), 3.18 (3H, s, 7-CH$_3$), 2.48, 2.25 (each 1H, m, 17-CH$_2$), 2.32, 2.13 (each 1H, m, 17^1-CH$_2$), 1.62 (3H, t, $J = 8$ Hz, 8^1-CH$_3$), 1.54 (3H, d, $J = 8$ Hz, 18-CH$_3$); MS (TOF) m/z 675 (M$^+$). **5**: Mp 221–222 °C; vis (toluene) $\lambda_{\max}$ 688 (relative intensity, 100%), 428 (85), 380 nm (70); MS (TOF) m/z 679 (M$^+$).

Bacteriochlorin 8. To a solution of **6** (12 mg, 0.022 mmol) in THF (5 mL) was added TMSCF$_3$ (=trifluoro(trimethylsilyl)methane, 250 mg, 1.76 mmol) and Bu$_4$NF•3H$_2$O (12 mg, 0.038 mmol), and the mixture was stirred for 1 min at room temperature. Ten percent aqueous HCl (2 mL) was added, and the reaction mixture was further stirred for 10 min. The mixture was poured into H$_2$O and extracted with CH$_2$Cl$_2$. The extract was washed successively with H$_2$O and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography (Et$_2$O–CH$_2$Cl$_2$, 3:17) to give **7** (4.2 mg, 31%, a 3^1-diastereomeric mixture) as a black solid: Mp 148–150 °C; vis (CH$_2$Cl$_2$) $\lambda_{\max}$ 731 (relative intensity, 58%), 519 (33), 382 (58), 353 nm (100); ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.62/8.53 (1H, s, 5-H), 8.31/8.30 (1H, s, 10-H), 8.17 (1H, s, 20-H), 6.41/6.37 (1H, br, 3-CH), 4.98, 4.81 (each 1H, d, $J = 19$ Hz, 13^1-CH$_2$), 4.20 (1H, br, 7-H), 4.16 (1H, br, 18-H), 3.99 (1H, br, OH), 3.96 (1H, br, 17-H), 3.92 (1H, br, 8-H), 3.60 (3H, s, COOCH$_3$), 3.37 (3H, s, 12-CH$_3$), 3.32/3.29 (3H, s, 2-CH$_3$), 2.48/2.12 (each 1H, m, 17-CH$_2$), 2.44/2.21 (each 1H, m, 17^1-CH$_2$), 2.31/2.02 (each 1H, m, 8-CH$_2$), 1.75/1.74 (3H, d, $J = 7$ Hz, 7-CH$_3$), 1.67/1.63 (3H, d, $J = 7$ Hz, 18-CH$_3$), 1.11/1.08 (3H, t, $J = 8$ Hz, 8^1-CH$_3$), 0.85/0.82 (1H, br s, NH), −0.58/−0.60 (1H, br s, NH); HRMS (FAB) m/z 623.2857 (MH$^+$), calcd for C$_{34}$H$_{37}$F$_3$N$_4$O$_4$ 623.2845.

To a solution of **7** (9.3 mg, 15 µmol) in CH$_2$Cl$_2$ (5 mL) were added (Pr$_4$N)[RuO$_4$] (1.1 mg, 3.0 µmol) and NMO (=4-methylmorpholine N-oxide) (7.0 mg, 60 µmol), and the mixture was stirred for 2 h at room temperature. The reaction was monitored by UV–vis spectrum. (Pr$_4$N)[RuO$_4$] (4.0 mg, 11 µmol) and NMO (24 mg, 200 µmol) were added and the mixture was stirred for 1 h, poured into 2% aqueous HCl and extracted with CH$_2$Cl$_2$. The extract was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography (Et$_2$O–CH$_2$Cl$_2$, 1:19) followed by HPLC (Cosmosil 5SL-II, 10 mm $\phi \times 250$ mm, acetone/1,2-dichloroethane = 1:19; 2.0 mL min^{-1}; t_{R} 11 min) to give methyl 3^2,3^2,3^2-trifluorobacteriopyropheophorbide-a (**8**) (5.2 mg, 56%) as a black solid: Mp 225–226 °C; vis (toluene) $\lambda_{\max}$ 775 (ε/M^{-1} cm^{-1}, 83000), 549 (22000), 369 nm (65000); ^{1}H NMR (CDCl$_3$, 600 MHz): δ 9.01 (1H, s, 5-H), 8.63 (1H, s, 20-H), 8.60 (1H, s, 10-H), 5.18, 5.02 (each 1H, d, $J = 20$ Hz, 13^1-CH$_2$), 4.37 (2H, m, 7-, 18-H), 4.20 (1H, dt, $J = 9$, 2 Hz, 17-H), 4.12 (1H, m, 8-H), 3.62 (3H, s, COOCH$_3$), 3.56 (3H, s, 2-CH$_3$), 3.50 (3H, s, 12-CH$_3$), 2.63, 2.23 (each 1H, m, 17-CH$_2$), 2.56, 2.28 (each 1H, m, 17^1-CH$_2$), 2.41, 2.11 (2H, m, 8-CH$_2$), 1.84 (3H, d, $J = 7$ Hz, 7-CH$_3$) 1.76 (3H, d, $J = 7$ Hz, 18-CH$_3$), 1.12 (3H, t, $J = 7$ Hz, 8^1-CH$_3$), −0.10, −1.32 (each 1H, br s, NH); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 195.7 (C13^1), 182.1 (q, $^2J_{\mathrm{C–F}} = 38$ Hz, C3^1), 173.4, 169.6, 167.1, 166.1, 159.7, 147.0, 141.2, 136.3, 136.0, 135.1, 131.6, 123.9, 123.6 (C1, 2, 3, 4, 6, 9, 11, 12, 13, 14, 16, 17^3, 19), 116.7 (q, $^1J_{\mathrm{C–F}} = 289$ Hz, C3^2), 109.1 (C15), 99.1 (C10), 97.3 (C20), 96.7 (C5), 55.7 (C8), 51.9 (C17), 51.7 (C17^5), 48.9, 48.2 (C7, 18), 47.9 (C13^2), 30.8 (C17^2), 30.1 (C8^1), 29.8 (C17^1), 23.3 (C18^1), 23.2 (C7^1), 12.8 (q, $^5J_{\mathrm{C–F}} = 4$ Hz, C2^1), 11.7 (C12^1), 10.8 (C8^2); ^{19}F NMR (CDCl$_3$, 564 MHz): δ −79.82 (s, 3^1-CF$_3$); HRMS (FAB) m/z 620.2595 (M$^+$), calcd for C$_{34}$H$_{35}$F$_3$N$_4$O$_4$ 620.2620.



Scheme 2. Synthesis of trifluoroacetylbacteriochlorin **8**.

Results and Discussion

Synthesis of New Chemosensors 3–5 and 8. Metal insertion[13] of free-base chlorin **1** gave three kinds of metallochlorins **3**–**5**, which appeared green in aprotic solvent. On the other hand, we have developed synthetic routes for introducing a series of functional groups at the 3-position of methyl bacteriopyropheophorbide-a.[12] Some kinds of oxidation such as 3-vinyl to formyl group were found to be applicable with a little alteration of the free-base bacteriochlorin macrocycles. Thus, 3-formylbacteriochlorin **6** (Scheme 2) was treated by the same procedure for the conversion of methyl pyropheophorbide-d possessing the 3-formyl group to chlorin **1** requiring an oxidation step.[11] The 3-formyl group of **6** was reacted with TMSCF$_3$ and the resulting silyl ether was cleaved by aq HCl[14] to give bacteriochlorin **7** in 31% yield. Oxidation of the secondary alcoholic group in **7** to the 3-carbonyl group in **8** was performed by (Pr$_4$N)[RuO$_4$] and NMO[15] in 56% yield. The bacteriochlorin ring was maintained during the oxidation, and the yield (22% for two steps) was similar to that of **1** from methyl pyropheophorbide-d. The solution color of **8** turned out to be pink with an intense Q$_y$ peak at 775 nm in toluene.

Optical Properties of Chemosensors 3–5 and 8. Absorption spectra of three kinds of chemosensors are shown in Figures 1a and 1b, and the spectral data are summarized in Table 1. Compared to free-base chlorin **1**, zinc–chlorin **3** showed a slight blue shift of the Q$_y$ peak, while bacteriochlorin **8** showed a large red-shift of the Q$_y$ peak together with blue shift of the Soret band. Because most of both the Soret and Q$_y$ bands are located out of the visible region, the intense Q$_x$ peak

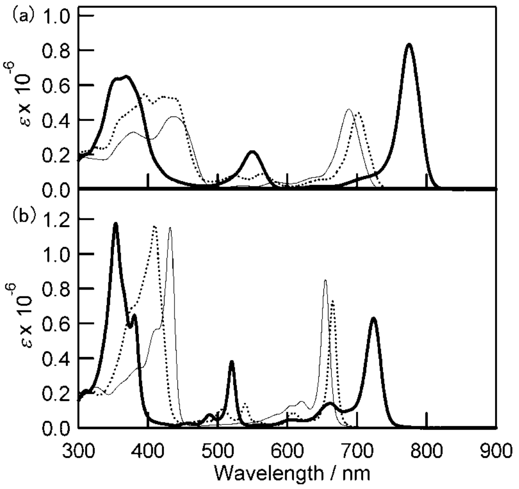


Figure 1. Electronic absorption spectra of chlorin **1** (solid thin line), zinc–chlorin **3** (dotted line), and bacteriochlorin **8** (solid thick line) in (a) toluene and (b) $BuNH_2$. Each spectrum was measured at 1.0×10^{-5} M.

Table 1. Absorption Maxima (λ_{max}/nm) and Fluorescent Emission Quantum Yield (QY/%) of Chlorin **1**, Zinc–Chlorin **3**, and Bacteriochlorin **8** in Toluene (Keto Form) and in $BuNH_2$ (α-Amino Alcohol Form)

Compound	Solvent	Soret	Q_x	Q_y	QY[a]
1	Toluene	395, 424, 438	525, 563	701	16
	$BuNH_2$	409	508, 539	665	21
3	Toluene	379, 437	—[b]	688	16
	$BuNH_2$	432	—[b]	655	19
4	Toluene	380, 421	—[b]	685	0.6
	$BuNH_2$	434	—[b]	650	3.2
5	Toluene	377, 428	—[b]	688	<0.1
	$BuNH_2$	425	—[b]	650	<0.1
8	Toluene	355, 369	549	775	7
	$BuNH_2$	353, 380	488, 520	724	12

a) Bacteriochlorin **8** in $BuNH_2$ was excited at 380 nm while other sample solutions were excited at 410 nm. b) Broad peak.

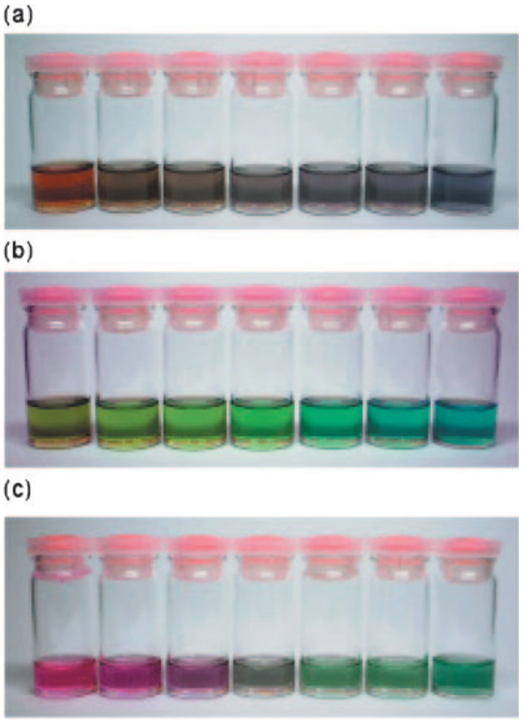


Figure 2. Solution color changes by α-amino alcohol formation of (a) chlorin **1**, (b) zinc–chlorin **3**, and (c) bacteriochlorin **8** at room temperature (20 °C). [Chemosensor] = 0.1 mM. Solution compositions are $[BuNH_2]$ = 0, 50, 100, 200, 500, and 1000 mM in toluene and in $BuNH_2$, from left to right, respectively.

of **8**, which is characteristic in bacteriochlorin derivatives, would be the main reason for the pink colorizing solution. In 1-aminobutane ($BuNH_2$), these chemosensors exist as their α-amino alcohol forms, and drastic spectral changes such as blue-shifts of the peak maxima and peak sharpening were observed. For example, Q_x/Q_y peaks of bacteriochlorin **8** shifted from 549/775 to 520/724 nm, and half-widths of peak maxima changed from 807/573 to 459/479 cm^{-1}, respectively. The equilibrium between keto forms and α-amino alcohol adducts exists in the presence of $BuNH_2$ in toluene, and caused visual color changes depending on the concentration of the amine. The complexation could also be monitored by fluorescence spectra,[11] although the quantum yield of **8** was smaller than those of chlorins **1** and **3**. Nickel and copper as the central metal of the chlorin ring strongly quenched the fluorescence. The pictures representing solution colors of three kinds of chemosensors are aligned in Figure 2. Brown solution of chlorin **1** gradually changed through dark gray to purple by addition of $BuNH_2$, zinc–chlorin **3** changed from green to blue, and bacteriochlorin **8** turned from pink to turquoise via pale gray. The color changes of nickel–chlorin **4** and copper–chlorin **5** were similar to that of **3** (Figures S7 and S8 in SI).

Thermodynamic Properties of the α-Amino Alcohol Formation. As a representative example, the equilibrium of chlorin **1** with $BuNH_2$ was examined by ^{1}H NMR spectrometry.[16] When $BuNH_2$ was added to a solution of **1** in toluene-d_8, the ^{1}H NMR spectrum showed signals of both trifluoroacetylchlorin **1** and its α-amino alcohol **2a**. Figure 3 shows the ^{1}H NMR spectra of three kinds of *meso*-protons of **1** in the presence of 26 equivalents of $BuNH_2$ measured at different temperatures. α-Amino alcohol form **2a** was dominant at room temperature (20 °C, **1**:**2a** = 0.05:1), but the ratio of **2a** decreased at higher temperatures and the adduct was almost dissociated at 80 °C (**1**:**2a** = 7.3:1). Thermodynamic parameters for the complexation were calculated as $\Delta H = -69\ kJ\,mol^{-1}$ and $\Delta S = -196\ J\,K^{-1}\,mol^{-1}$ based on the van't Hoff plot as shown in Figure 4. This NMR experiment shows the fact that the equilibrium can almost be shifted from one to the other by changing the solution temperature from 20 to 80 °C, which also led to another interesting character of the chemosensors. Figure 5 demonstrates the thermochromism of this solution system.[17] The solution of chemosensor **8** with excess $BuNH_2$ in toluene appears turquoise due to the α-amino alcohol formation at room temperature. When the test tube containing this solution system was immersed in a hot water bath, the color changed to pink as expected, and the heating–cooling cycles can be repeated with visual color changes. It should be noted

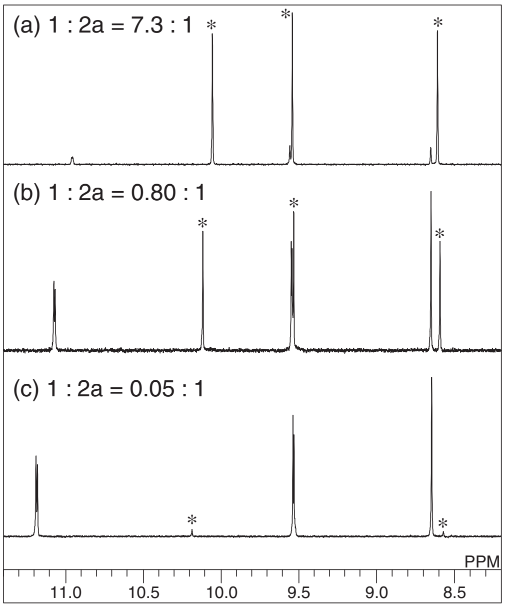


Figure 3. Selected region of the ^{1}H NMR spectra of chlorin **1** in the presence of 26 equivalents of $BuNH_2$ in toluene-d_8 at (a) 80, (b) 50, and (c) 20 °C. *meso*-Protons of the trifluoroacetyl form **1** are indicated by asterisk (*).

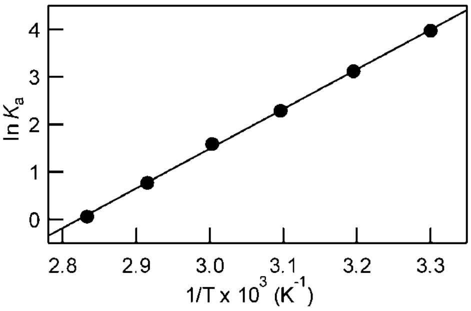


Figure 4. van't Hoff plot of the equilibrium between trifluoroacetylchlorin **1** and its α-amino alcohol **2a**. Association constants ($K_a = [\mathbf{2a}]/[\mathbf{1}][n\text{-}BuNH_2]$ in toluene-d_8) were calculated by integration values of their ^{1}H NMR peaks at the measured temperature.

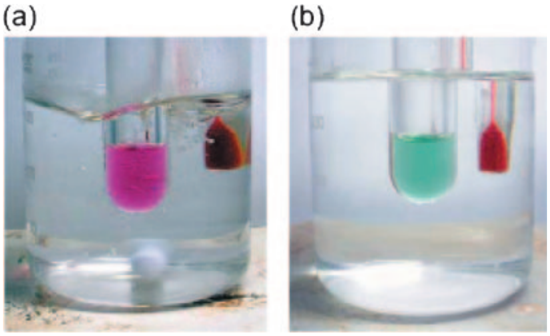


Figure 5. Thermochromism of the equilibrium between bacteriochlorin **8** and its α-amino alcohol with $BuNH_2$. Test tube of the sample solution, $[\mathbf{8}] = 0.1$ mM and $[BuNH_2] = 1$ M in toluene, was immersed in (a) a hot water bath at 80 °C and (b) a cold water bath at 20 °C.

that the equilibrium is slow enough on a NMR-timescale to distinguish two kinds of species (Figure 3), while the thermochromic phenomena appeared to be completed within several seconds.[18]

Conclusion

We have developed synthetic routes for converting natural chlorophylls to chemosensors of amine detection. The functional dyes would be applicable as sensing components of optode membrane,[1,6,7a,7b] and the procedures demonstrated in this study should also be useful for synthetic studies of bacteriochlorin derivatives.[13,19]

This work was partially supported by Grants-in-Aid for Scientific Research (B) (No. 19350088) from the Japan Society for the Promotion of Science (JSPS) and Young Scientists (No. 18750124) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government, as well as by the "Academic Frontier" Project for Private Universities: matching fund subsidy from MEXT, 2003–2007.

Supporting Information

^{1}H/^{13}C NMR spectra of **3** in 1% pyridine-d_5/$CDCl_3$, ^{1}H NMR spectra of **4** and **7** in $CDCl_3$, and ^{1}H/^{13}C NMR spectra of **8** in $CDCl_3$ (Figures S1–S6), solution color changes of **4** and **5** in toluene with addition of $BuNH_2$ (Figures S7 and S8), and thermochromism of **1** and **3** with $BuNH_2$ in toluene (Figures S9 and S10). This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

References

1 E. Bakker, P. Bühlmann, E. Pretsch, *Chem. Rev.* **1997**, *97*, 3083.

2 For reviews, see: a) C. Suksai, T. Tuntulani, *Chem. Soc. Rev.* **2003**, *32*, 192. b) R. Martínez-Máñez, F. Sancenón, *Chem. Rev.* **2003**, *103*, 4419. c) T. W. Bell, N. M. Hext, *Chem. Soc. Rev.* **2004**, *33*, 589. d) P. A. Gale, *Acc. Chem. Res.* **2006**, *39*, 465. e) F. P. Schmidtchen, *Coord. Chem. Rev.* **2006**, *250*, 2918. f) E. A. Katayev, Y. A. Ustynyuk, J. L. Sessler, *Coord. Chem. Rev.* **2006**, *250*, 3004.

3 For recent examples of chemosensors, see: a) D. Citterio, J. Takeda, M. Kosugi, H. Hisamoto, S. Sasaki, H. Komatsu, K. Suzuki, *Anal. Chem.* **2007**, *79*, 1237. b) N. Singh, D. O. Jang, *Org. Lett.* **2007**, *9*, 1991. c) W. Liu, L. Xu, R. Sheng, P. Wang, H. Li, S. Wu, *Org. Lett.* **2007**, *9*, 3829. d) R. E. Gawley, H. Mao, M. M. Haque, J. B. Thorne, J. S. Pharr, *J. Org. Chem.* **2007**, *72*, 2187. e) Q. Zeng, P. Cai, Z. Li, J. Qin, B. Z. Tang, *Chem. Commun.* **2008**, 1094. f) W. Shi, H. Ma, *Chem. Commun.* **2008**, 1856. g) J. Killoran, S. O. McDonnell, J. F. Gallagher, D. F. O'Shea, *New J. Chem.* **2008**, *32*, 483. h) X. Chen, Z. Li, Y. Xiang, A. Tong, *Tetrahedron Lett.* **2008**, *49*, 4697. i) J.-J. Lee, B. C. Noll, B. D. Smith, *Org. Lett.* **2008**, *10*, 1735. j) Y. Liu, M. Han, H.-Y. Zhang, L.-X. Yang, W. Jiang, *Org. Lett.* **2008**, *10*, 2873. k) M. Yuan, W. Zhou, X. Liu, M. Zhu, J. Li, X. Yin, H. Zheng, Z. Zuo, C. Ouyang, H. Liu, Y. Li, D. Zhu, *J. Org. Chem.* **2008**, *73*, 5008. l) H.-W. Rhee, C.-R. Lee, S.-H. Cho, M.-R. Song, M. Cashel, H. E. Choy, Y.-J. Seok, J.-I. Hong, *J. Am. Chem. Soc.* **2008**, *130*, 784.

4 P. Bühlmann, E. Pretsch, E. Bakker, *Chem. Rev.* **1998**, *98*, 1593.

5 a) H. J. Lee, I. J. Yoon, C. L. Yoo, H.-J. Pyun, G. S. Cha, H. Nam, *Anal. Chem.* **2000**, *72*, 4694. b) S. Makarychev-Mikhailov, O. Goryacheva, J. Mortensen, A. Legin, S. Levitchev, Y. Vlasov, *Electroanalysis* **2003**, *15*, 1291.

6 a) G. J. Mohr, D. Citterio, C. Demuth, M. Fehlmann, L. Jenny, C. Lohse, A. Moradian, T. Nezel, M. Rothmaier, U. E. Spichiger, *J. Mater. Chem.* **1999**, *9*, 2259. b) G. J. Mohr, *Sens. Actuators, B* **2003**, *90*, 31.

7 a) G. J. Mohr, C. Demuth, U. E. Spichiger-Keller, *Anal. Chem.* **1998**, *70*, 3868. b) G. J. Mohr, N. Tirelli, C. Lohse, U. E. Spichiger-Keller, *Adv. Mater.* **1998**, *10*, 1353. c) E. Mertz, J. B. Beil, S. C. Zimmerman, *Org. Lett.* **2003**, *5*, 3127. d) E. Mertz, S. C. Zimmerman, *J. Am. Chem. Soc.* **2003**, *125*, 3424. e) E. Mertz, S. L. Elmer, A. M. Balija, S. C. Zimmerman, *Tetrahedron* **2004**, *60*, 11191. f) M. Matsui, K. Yamada, K. Funabiki, *Tetrahedron* **2005**, *61*, 4671. g) S. Reinert, G. J. Mohr, *Chem. Commun.* **2008**, 2272.

8 a) Y. K. Kim, Y.-H. Lee, H.-Y. Lee, M. K. Kim, G. S. Cha, K. H. Ahn, *Org. Lett.* **2003**, *5*, 4003. b) Y. M. Chung, B. Raman, D.-S. Kim, K. H. Ahn, *Chem. Commun.* **2006**, 186.

9 a) S. Sasaki, A. Hashizume, D. Citterio, E. Fujii, K. Suzuki, *Angew. Chem., Int. Ed.* **2002**, *41*, 3005. b) S. Sasaki, G. Monma, D. Citterio, K. Yamada, K. Suzuki, *Chimia* **2005**, *59*, 204.

10 G. J. Mohr, U.-W. Grummt, *J. Fluoresc.* **2006**, *16*, 185.

11 S. Sasaki, Y. Kotegawa, H. Tamiaki, *Tetrahedron Lett.* **2006**, *47*, 4849.

12 S. Sasaki, H. Tamiaki, *J. Org. Chem.* **2006**, *71*, 2648.

13 H. Tamiaki, M. Amakawa, A. R. Holzwarth, K. Schaffner, *Photosynth. Res.* **2002**, *71*, 59.

14 a) G. Li, Y. Chen, J. R. Missert, A. Rungta, T. J. Dougherty, Z. D. Grossman, R. K. Pandey, *J. Chem. Soc., Perkin Trans. 1* **1999**, 1785. b) R. P. Singh, J. M. Shreeve, *Tetrahedron* **2000**, *56*, 7613.

15 a) S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639. b) H. Tamiaki, S. Yagai, T. Miyatake, *Bioorg. Med. Chem.* **1998**, *6*, 2171.

16 Thermodynamic parameters for the complexation between **1** and BuNH$_2$ in CDCl$_3$ were determined to be $\Delta H = -48$ kJ mol^{-1} and $\Delta S = -147$ J K^{-1} mol^{-1}, based on ^{1}H NMR measurements at various temperatures, while the association constant in THF was determined to be 7.8×10^3 M^{-1} at 20 °C based on electronic absorption titration method, see Ref. 11.

17 For the pictures of temperature-dependent color changes in **1** and **3** with BuNH$_2$ in toluene, see Figures S9 and S10 in SI.

18 When the test tube was immersed into beakers of boiling- and ice-water with shaking, the thermochromism was completed within a few seconds.

19 Synthetic chlorophyll derivatives possessing a bacteriochlorin π-system are available from limited papers: a) R. K. Pandey, G. Zheng, in *The Porphyrin Handbook*, ed. by K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, San Diego, **2000**, Vol. 6, pp. 157–230. b) Y. Chen, G. Li, R. K. Pandey, *Curr. Org. Chem.* **2004**, *8*, 1105. c) M. Kunieda, T. Mizoguchi, H. Tamiaki, *Photochem. Photobiol.* **2004**, *79*, 55. d) M. Kunieda, T. Mizoguchi, H. Tamiaki, *Tetrahedron* **2004**, *60*, 11349. e) Y. Chen, A. Sumlin, J. Morgan, A. Gryshuk, A. Oseroff, B. W. Henderson, T. J. Dougherty, R. K. Pandey, *J. Med. Chem.* **2004**, *47*, 4814. f) A. F. Mironov, M. A. Grin, A. G. Tsiprovskii, R. A. Titeev, E. A. Nizhnik, I. S. Lonin, *Mendeleev Commun.* **2004**, *14*, 204. g) M. Kunieda, H. Tamiaki, *J. Org. Chem.* **2005**, *70*, 820. h) A. Gryshuk, Y. Chen, L. N. Goswami, S. Pandey, J. R. Missert, T. Ohulchanskyy, W. Potter, P. N. Prasad, A. Oseroff, R. K. Pandey, *J. Med. Chem.* **2007**, *50*, 1754, and Ref. 13.