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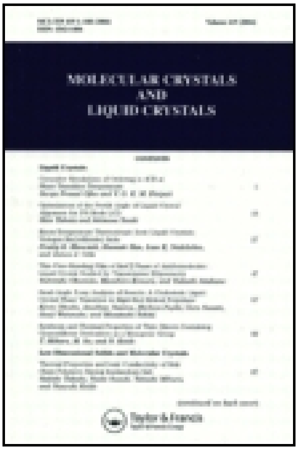

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Absorption and Emission Properties of Acenaphthoporphyrins

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*Acenaphtho[1,2-*b*]porphyrins (AcePs) were prepared by the [3 + 1] condensation method and their photochemical properties were investigated. The fluorescence spectra of the free-base AcePs in $CHCl_3$ showed two emission bands at 660 and 720 nm, whose intensity drastically changed depending on the excitation wavelength. However, those of zinc complexes did not show such a wavelength dependence and showed similar emission spectra by the excitation at various wavelengths. The fluorescence excitation spectra and quantum yields of the free-base AcePs in $CHCl_3$ showed the similar excitation wavelength dependence. This fact indicates that two electronic structures exist in the free-base AcePs and their fluorescence is emitted from one structure in higher quantum yield ($\lambda_{EM} = 660$ nm) and from the other in lower yield ($\lambda_{EM} = 720$ nm), respectively.*

Keywords: absolute quantum yield; acenaphtho[1,2-b]porphyrin; fluorescence emission; fluorescence excitation; NH tautomer

The π-conjugated porphyrins with exocyclic aromatics have been extensively studied because of their special optical and electrical properties [1]. It is well known that porphyrin molecules present two absorption bands in the visible spectra, Soret (S_0–S_2 transition) and Q (S_0–S_1 transition) bands, which are observed at around 400 nm and at 500–650 nm, respectively. In general, fluorescence of porphyrins is emitted from Q bands and shows similar spectrum shape unrelated to the excitation wavelength. Recently, a few reports have been published for the excitation wavelength dependence of fluorescence for π-expanded porphyrins with substituents at 5,15-*meso*-positions [2,3].

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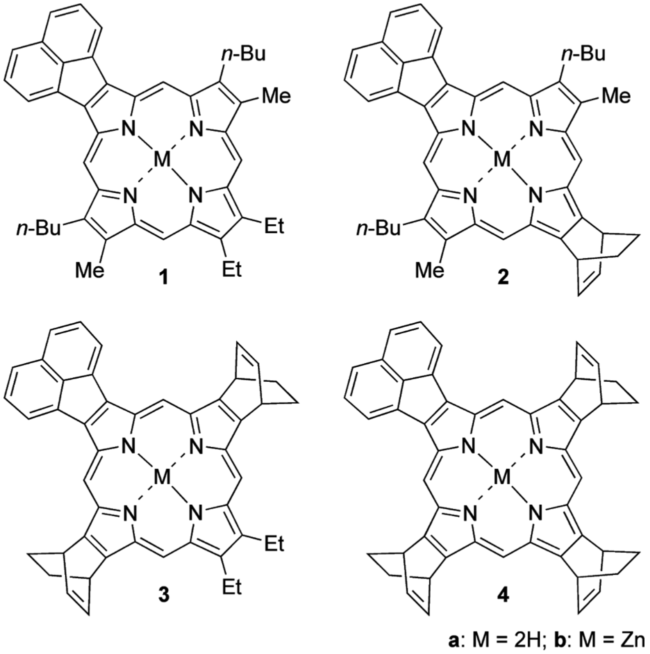

CHART 1 Molecular structures of porphyrins used.

Independently, we have found a drastic change of the fluorescence spectra depending on the excitation wavelength for acenaphtho[1,2-*b*]porphyrins (AcePs), for which π-expansion was achieved with exocyclic aromatics at β-position of pyrrole. Herein, we report the preparation of a series of AcePs and their unique photophysical properties.

Tripyrranes containing acenaphtho[1,2-*c*]pyrrole were prepared by the montmorillonite K-10 catalyzed condensation and used in following reactions without further purification after work-up [4]. The [3 + 1] condensation of tripyrrane and pyrrole afforded novel BCOD-fused AcePs **2a** and **3a** together with β-alkyl AceP **1a** and tri(BCOD)AceP **4a** [5,6]. These porphyrins were converted into the corresponding zinc complexes **1b**–**4b** on treatment with zinc acetate (Chart 1).

Free-base AcePs **1a**–**4a** showed different absorption spectra depending on the β-substituents as shown in Figure 1. Two strong bands were observed at 430 and 565 nm for *adj*-β-BCOD type of AcePs **3a** and **4a**. For *adj*-β-alkyl AcePs **1a** and **2a**, these bands became weaker and the bands at 385, 455, and 530 nm became stronger compared to **3a** and **4a**.

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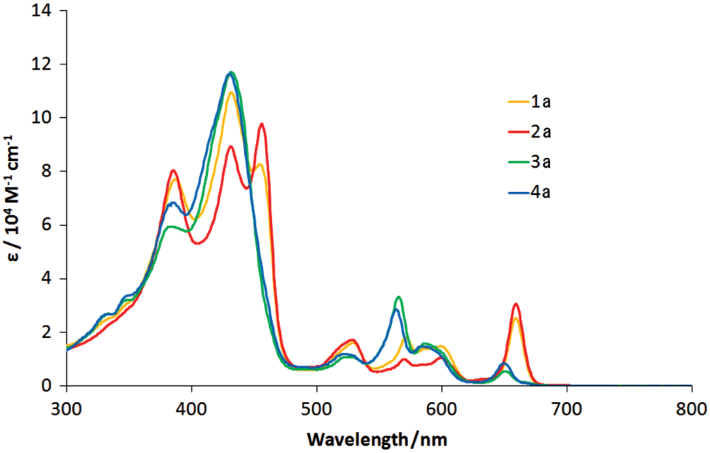

FIGURE 1 Absorption spectra of **1a** (orange line), **2a** (red line), **3a** (green line), and **4a** (blue line) in $CHCl_3$.

The absorption and fluorescence spectra of **3a** and **3b** in $CHCl_3$ are shown in Figure 2. The fluorescence spectra of **3a** with excitation wavelength (λ_{EX}) at 460 or 530 nm showed a strong band at 660 nm and a weaker band at 720 nm. However, when λ_{EX} was 420 or 565 nm, the emission peak at 660 nm became weaker and that of 720 nm became stronger. On the other hand, such an excitation wavelength dependence of fluorescence was not observed for zinc complex **3b**, where the wavelength and relative intensity of fluorescence emission were similar even though the excitation wavelength was changed, as shown in Figure 2(b). The similar influence of excitation wavelength was observed for the fluorescence spectra of the other AcePs **1**, **2**, and **4**.

In Figure 3(d), the absorption spectrum of **3a** and its absolute quantum yields (Φ_F) in $CHCl_3$ are plotted against λ_{EX}. These Φ_F values were determined on a Hamamatsu Photonics K.K. absolute PL quantum yield measurement system C9920–03. The emissions of **3a** ($\lambda_{EX} = 460$ or 530 nm) was observed at mainly 660 nm with Φ_F values of 0.10–0.12, while the main λ_{EM} ($\lambda_{EX} = 420$ or 565 nm) was 720 nm and Φ_F values are 0.02–0.05 (Figs. 2(a) and 3(d)). Therefore, Φ_F values of the emissions from 660 and 720 nm looks different. The free-base AcePs **1a**, **2a**, and **4a** also showed high and low Φ_F values depending on λ_{EX} as summarized in Table 1. On the other hand, Φ_F's of the zinc complexes **1b–4b** were constant values regardless of the λ_{EX} (Fig. 4(c) for **3b**).

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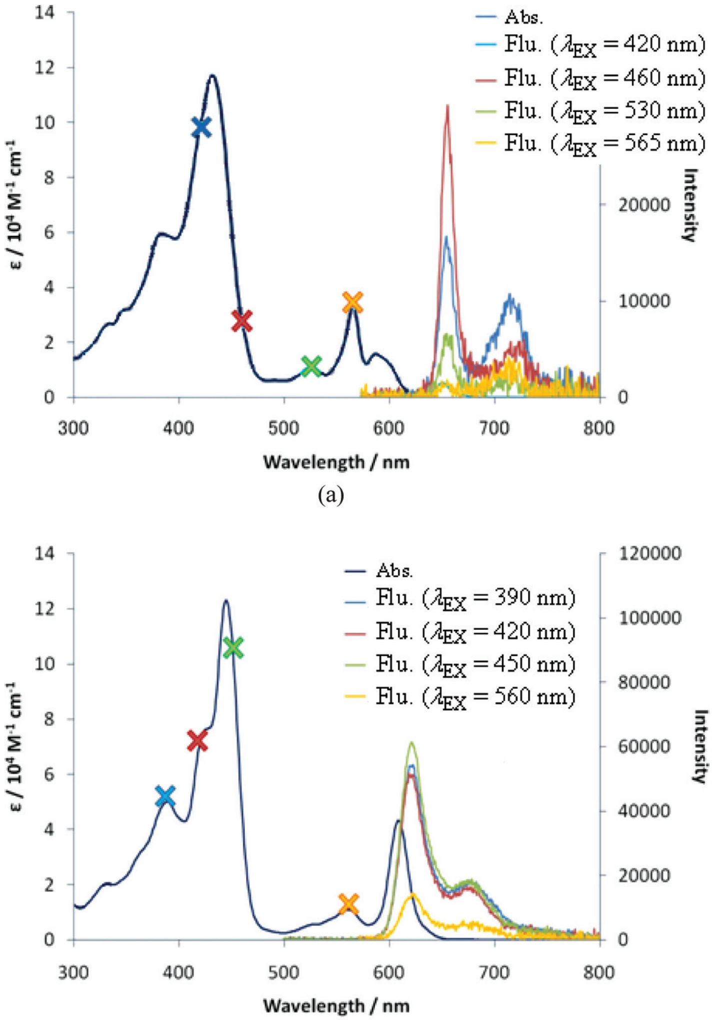

(a)

(b)

FIGURE 2 Absorption (dark blue line) and fluorescence emission (blue, red, green and yellow lines) spectra of (a) **3a** (1 μM) and (b) **3b** (1 μM) in $CHCl_3$. ×: excitation wavelength. Colors of lines are corresponding to the color of ×.

The fluorescence excitation spectra of **3a** and **3b** in $CHCl_3$ are shown in Figures 3 and 4, respectively. In excitation spectrum of **3a** ($\lambda_{EM} = 655\,nm$), three bands were observed at around 380, 460, and 530 nm (Fig. 3(a)), which were consistent with the wavelength of

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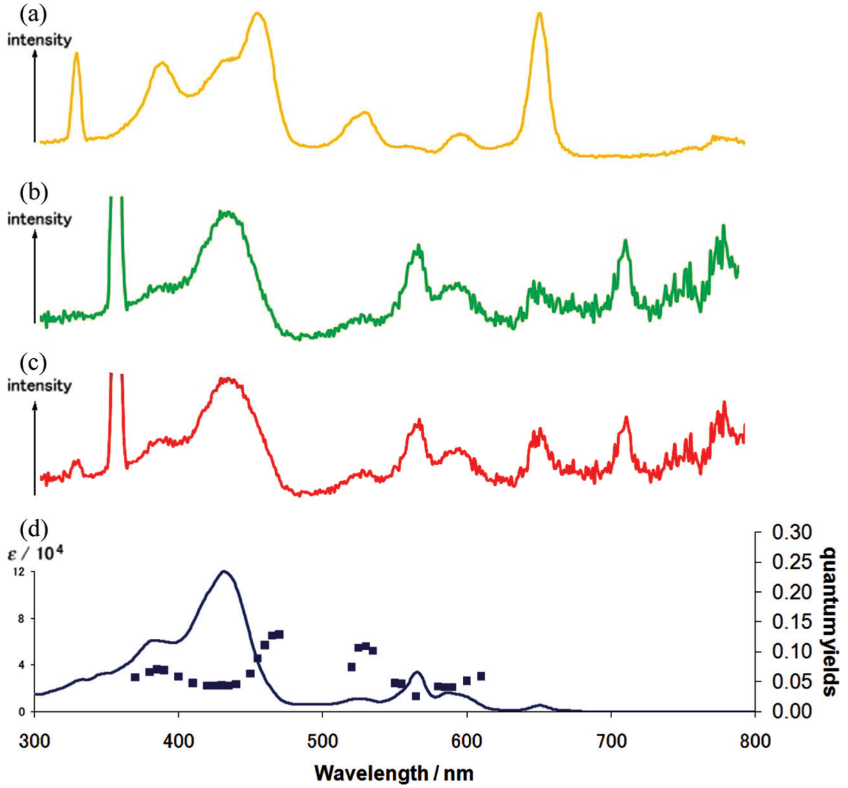

FIGURE 3 Fluorescence excitation ((a) orange line: $\lambda_{EM} = 655$ nm; (b) green line: $\lambda_{EM} = 710$ nm; 1 μM), (c) combination of (a) and (b) in a ratio of 1:5 (red line), and (d) absorption (blue line) spectra in $CHCl_3$ and Φ_F versus λ_{EX} plots of **3a**.

TABLE 1 Absolute Quantum Yields of AcePs **1–4**

	Φ_F					Φ_F			
λ_{EX}/nm	420	460	530	565		390	420	450	560
1a	0.097	0.190	0.205	0.096[a]	**1b**	0.082	0.075	0.078	0.090
2a	0.130	0.188	0.188	0.088	**2b**	0.093	0.084	0.089	0.104
3a	0.043	0.111	0.109	0.025	**3b**	0.088	0.078	0.079	0.101
4a	0.060	0.137	0.110[b]	0.033	**4b**	0.096	0.088	0.086	0.091

[a] $\lambda_{EX} = 560$ nm.
[b] $\lambda_{EX} = 525$ nm.

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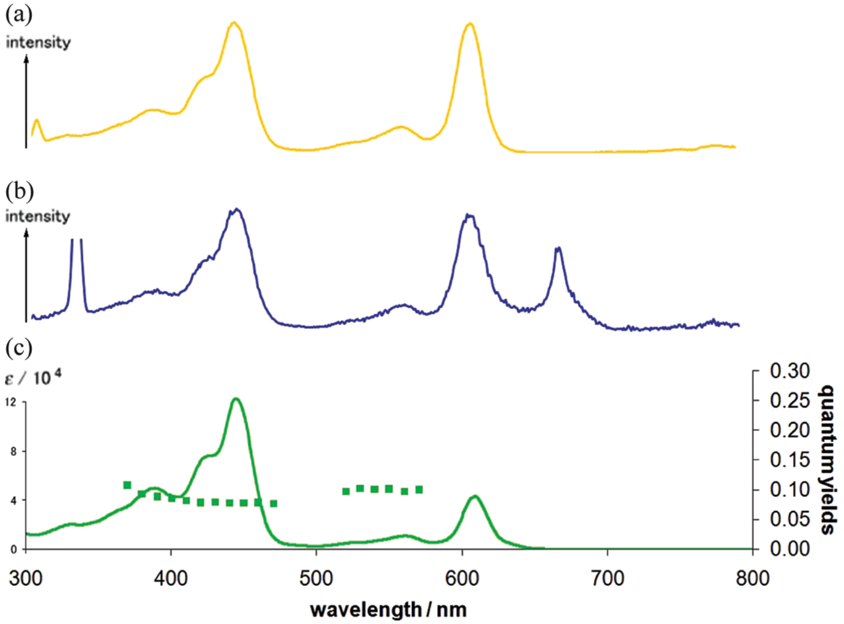

FIGURE 4 Fluorescence excitation ((a) orange line: $\lambda_{EM} = 615$ nm; (b) blue line: $\lambda_{EM} = 670$ nm; 1 μM), and (c) absorption (green line) spectra in $CHCl_3$ and Φ_F versus λ_{EX} plots of **3b**.

higher Φ_F values in Figure 3(d). Similarly, for excitation spectrum of **3a** ($\lambda_{EM} = 710$ nm), two bands appeared at around 440 nm and 570 nm (Fig. 3(b)), which were consistent with the wavelength of lower Φ_F values in Figure 3(d). When two excitation spectra ($\lambda_{EM} = 655$ and 710 nm) were combined in a ratio of 1:5, respectively, the obtained spectrum was almost same with the absorption spectrum (Figs. 3(c) and (d)). The excitation spectrum of **3b** ($\lambda_{EM} = 615$ nm) was similar

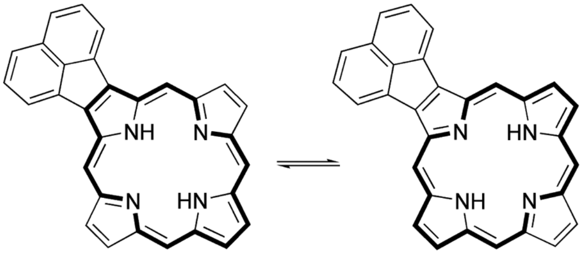

FIGURE 5 NH tautomers of AceP.

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to that of $\lambda_{EM} = 670\,\text{nm}$, and both were very similar to the absorption spectrum (Fig. 4). The reason of the λ_{EX} dependence of free-base porphyrins has not been clear, but slow exchange between two types of isomers such as NH tautomers as illustrated in Figure 5 might contribute to the photophysical properties in the solution, because such phenomenon was only observed for free-base AcePs, but not for zinc complexes.

In summary, a series of free-base AcePs **1a–4a** and their zinc complexes were synthesized. For the free-base AcePs there are two kinds of fluorescence spectra with different Φ_F values depending on the λ_{EX} in $CHCl_3$ solution. On the other hand, zinc complexes **1b–4b** did not exhibit such photophysical properties. The reason of the λ_{EX} dependence of free-base AcePs has not been clear and further work on confirming the mechanism is under way.

REFERENCES

[1] Lash, T. D. (2000). Syntheses of novel porphyrinoid chromophores. In: *The Porphyrin Handbook*, Kadish, K. M., Smith, K. M., & Guilard, R. (Eds.), Academic Press: San Diego, Vol. 2, Chapter 10, 125.

[2] Uttamlal, M. & Holmes-Smith, A. S. (2008). *Chem. Phys. Lett.*, *454*, 223.

[3] Jiang, L., Jiu, T., Li, Y., Li, Y., Yang, J., Li, J., Li, C., Liu, H., & Song, Y. (2008). *J. Phys. Chem. B*, *112*, 756.

[4] Boudif, A. & Momenteau, M. (1996). *J. Chem. Soc., Perkin Trans.*, *1*, 1235.

[5] Lash, T. D., Chandrasekar, P., Osuma, A. T., Chaney, S. T., & Spence, J. D. (1998). *J. Org. Chem.*, *63*, 8455.

[6] Okujima, T., Komobuchi, N., Uno, H., & Ono, N. (2006). *Heterocycles*, *67*, 255.