

A Novel Supramolecular Multicolor Thermometer by Self-Assembly of a π -Extended Zinc Porphyrin Complex

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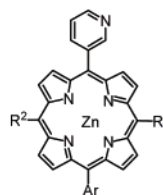
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Thermochromism is an interesting phenomenon, which can be applicable to the development of imaging and sensing materials. Classical examples include metal salts such as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, which displays a color change from pink to blue upon heating, as the result of thermal-induced coordination dynamics in aqueous media.¹ π -Conjugated polymers are also candidates for thermochromic materials. For example, polythiophene displays a thermoreversible color change between red and yellow in solution, due to a change in π -electronic conjugation by thermal-induced conformational dynamics of the backbone.² Although a variety of thermochromic systems have so far been reported,³ there are only limited examples that are capable of developing multiple colors at ambient temperatures. We now report a novel thermochromic system, via the self-assembly of a π -extended zinc porphyrin complex with a metal-ligating 3-pyridyl group (**1**).^{4,5} This system exhibits a multicolor thermochromism upon heating, for example, from 0 to 100 °C, by taking advantage of the absorption spectral change capability of **1** due to thermal-induced axial coordination dynamics. Therefore, **1** can be used as a multicolor thermometer.

As shown in Figure 1a, the zinc complex of 5-(3-pyridyl)-10-trimethylsilylethynyl-15-(3,5-dioctyloxyphenyl)porphyrin (**1**) in toluene displayed a stepwise color change from green to yellow to red on heating from 0 to 50 to 100 °C, respectively. The absorption spectrum of **1** was temperature-dependent in toluene (Figure 2a).⁶ At a low temperature such as 0 °C, **1** showed a split Soret absorption band with λ_{max} values of 428 and 443 nm, and displayed Q-bands at 571 and 610 nm. On the other hand, upon heating, the Soret-band at 428 nm was intensified at the expense of the 443-nm band, while the Q-bands were both blue-shifted to 558 and 595 nm. In sharp contrast, in the presence of a coordinating base such as pyridine (5%), the system displayed neither temperature-dependent spectral change nor thermochromic response, where the Soret-band did not show any splitting even at low temperatures.

A crystallographic study showed that the split absorption band in the Soret region is most likely due to an exciton coupling of self-assembled **1**.⁷ Although an attempt to grow crystals of **1** was unsuccessful, an analogous zinc complex of 5-(3-pyridyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (**4**) gave single crystals appropriate for X-ray crystallography.⁸ In the crystal structure (Figure 3), **4** adopts a cyclic tetramer via the axial coordination of the 3-pyridyl groups to the zinc porphyrin moieties ($\text{N}-\text{Zn} = 2.15 \text{ \AA}$), where the inner pyridyl (Py) groups are in contact with one another via a $\pi-\pi$ interaction (plane-to-plane separation = 3.40–3.43 Å). Such a sterically congested assembly appears to give rise to a considerable structural distortion, as the zinc porphyrin–pyridine dihedral angles are 103° (inner Py) and 74° (outer Py), which are much deviated from an ideal value of 90°.



- 1: $\text{R}^1 = \text{t-TMS}$, $\text{R}^2 = \text{H}$, $\text{Ar} = 3,5\text{-dioctyloxyphenyl}$
 2: $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{Ar} = 3,5\text{-di-}t\text{-butylphenyl}$
 3: $\text{R}^1 = \text{R}^2 = \text{t-TMS}$, $\text{Ar} = 3,5\text{-dioctyloxyphenyl}$
 4: $\text{R}^1 = \text{R}^2 = \text{Ar} = 3,5\text{-di-}t\text{-butylphenyl}$

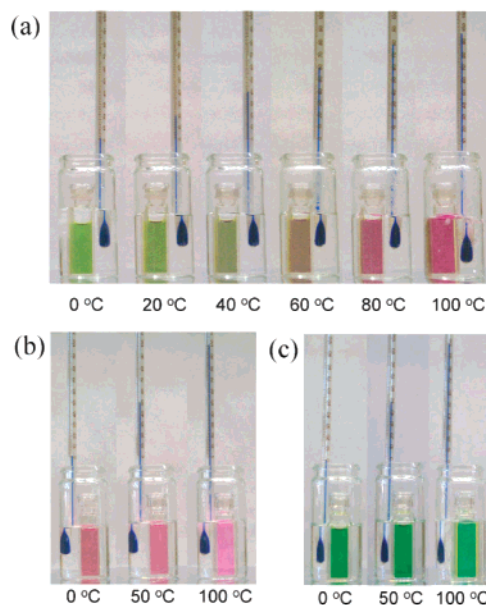


Figure 1. Temperature-dependent color changes of **1** (a), **2** (b), and **3** (c) in toluene ($9.8 \times 10^{-5} \text{ M}$).

Cold-spray ionization mass spectrometry (CSI-MS)⁹ of a CHCl_3 solution of **1** showed a strong peak at $m/z = 3518$ corresponding to the tetramer of **1** ($[\mathbf{1}_4]^+$, Figure 4), in addition to some minor peaks at 2639, 1759, and 1319, assignable to $[\mathbf{1}_3]^+$, $[\mathbf{1}_2]^+$ and/or $[\mathbf{1}_4]^{2+}$, and $[\mathbf{1}_3]^{2+}$, respectively. This result indicates that **1** preferentially adopts a cyclotetrameric structure in solution. ¹H NMR spectroscopy of **1** in CDCl_3 at 30 °C showed broaden signals possibly due to the presence of several slowly interconverting stereoisomers upon cyclotetramerization of **1**. However, compound **2** without an alkynyl group under similar conditions displayed a relatively sharp ¹H NMR spectrum, where the pyridyl groups showed eight different signals at δ 2.27, 2.89, 3.19, 4.23, 5.45, 5.94, 6.77, and 7.14 ppm. These signals are upfield shifted and characteristic of the cyclotetrameric structure, because the cyclic tetramer of **2** bears two inequivalent sets of pyridyl groups in close proximity to the zinc porphyrin moieties and should display totally eight inequivalent Py signals with identical integral values.

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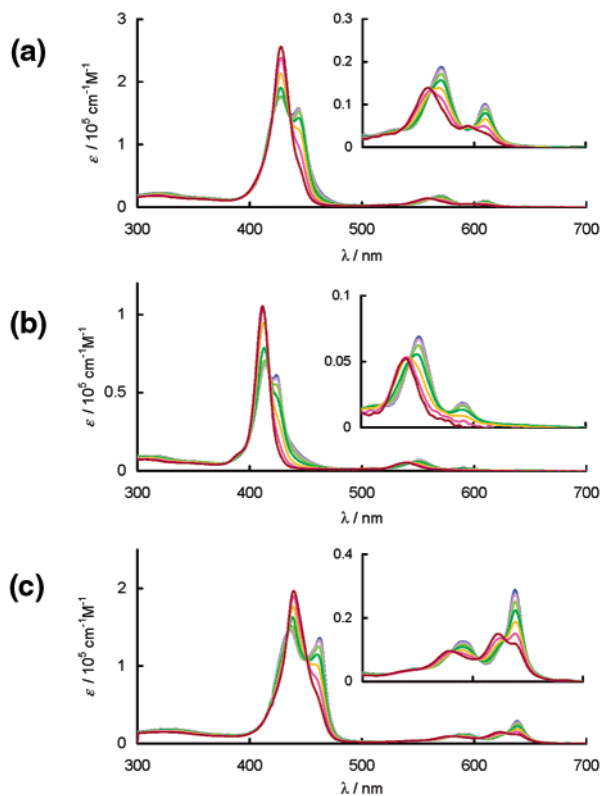


Figure 2. Variable-temperature absorption spectral profiles of **1** (a), **2** (b), and **3** (c) in toluene (9.8×10^{-5} M) at 0–100 °C (blue, 0 °C; red, 100 °C). Insets show magnified spectra in the Q-band region.

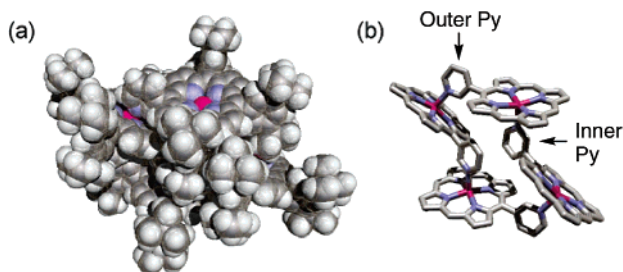


Figure 3. X-ray crystal structure of **4**. (a) CPK representation. (b) Stick representation, where 3,5-di-*tert*-butylphenyl groups and hydrogen atoms are omitted for clarity.

We also found that the alkynyl group of **1** plays a crucial role in the vivid thermochromic response (Figure 1a). Although **2** and **3** both showed temperature-dependent absorption spectral changes (Figure 2b and c, respectively), **2** without any alkynyl group, on heating, developed only a small color change from orange to pink (Figure 1b), while **3** having two alkynyl groups stayed in green over a wide temperature range (Figure 1c).¹⁰ Generally, absorption of lights in ranges of 430–490, 490–560, and 560–800 nm provides complementary colors of yellow-orange, red-reddish purple, and blue-green, respectively. Introduction of a single alkynyl group at the meso-position of compound **2** (Q-band region; 520–600 nm) allows an appropriate shift of the absorption band of the complex (Q-band of **1**; 530–630 nm), so that the association/dissociation dynamics can be detected as a vivid switching between warm and cold colors by human eyes. On the other hand, when two alkynyl groups are introduced as in the case of compound **3**,

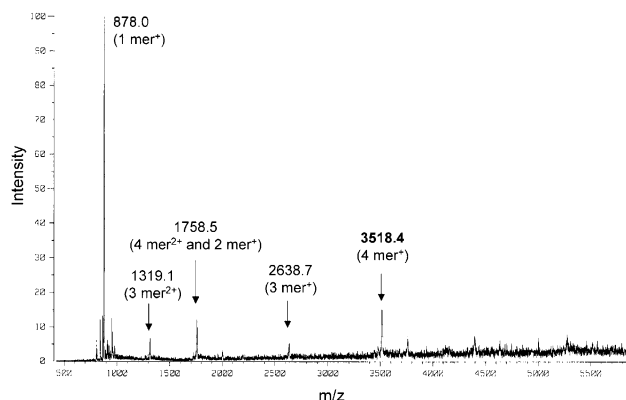


Figure 4. Cold-spray ionization mass spectrum of a CHCl_3 solution of **1**.

the absorption bands are entirely shifted to a green region (550–660 nm), irrespective of whether the zinc porphyrin is assembled or not.

In conclusion, we have demonstrated the first example of supramolecular thermochromism of metalloporphyrin by using a zinc complex of (3-pyridyl)porphyrin with an alkynyl sidearm (**1**). Because of an appropriate extension of π -electronic conjugation of the porphyrin chromophore, the thermal-induced self-assembling dynamics of **1** can be detected as a vivid color change from red to yellow to green. The present work will provide a novel molecular design concept for supramolecular thermometers.

Acknowledgment. The present work was sponsored by a Grants-in-Aid for Scientific Research (No. 15350128) and Encouragement of Young Scientists (No. 15750028) from the ministry of Education, Science, Sports, and Culture, Japan. A.T. thanks the Mizuho Foundation for the Promotion of Sciences and the Foundation Advanced Technology Institute.

Supporting Information Available: Experimental details for the synthesis of **1–4**. X-ray crystallographic data for **4** (CIF). Absorption spectra of **1** at different concentrations. VT-absorption spectra of **1** in toluene containing 5% pyridine. Variable-temperature ^1H NMR spectral profile of **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) The ^1H NMR spectral pattern of **3** was similar to that of **2**, suggesting that **3** also adopts a cyclotetrameric structure (see Supporting Information 4).

JA038349K