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Core-modified phthalocyanine analogues with a seven-membered ring unit in place of a five-membered ring unit

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ABSTRACT

A variety of phthalocyanine analogues with a seven-membered ring unit in place of a five-membered ring unit were synthesized from aromatic dicarbonitriles bearing cyano groups at 1,4-separate positions. Based on the spectroscopic analyses and theoretical calculations, tetraazachlorine-like electronic structures of these novel compounds stemming from severe twist of the conjugation system at the seven-membered ring unit have been revealed.

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Phthalocyanine 1 has been broadly utilized as blue and green dyes and pigments, and has recently attracted much attention as functional molecules in a variety of areas of photo-energy conversion and molecular electronics because of their intense absorption of the UV/vis light and planar macrocyclic 18π-conjugation systems.^{1,2} Core-modification, that is replacement of isoindole units with other hetero-aromatic ring units, is a potentially promising modification method, but has been rarely investigated mainly due to synthetic difficulties.³ Recently we succeeded in the syntheses of core-modified phthalocyanine analogues with six- or sevenmembered ring units in place of five-membered ring units of the isoindole moieties (Chart 1) by using aromatic dicarbonitriles, which possess cyano groups at 1,3- or 1,4-separate positions, and significant changes of their electronic structures from those of regular phthalocyanines were also revealed.^{4,5} The absorption spectra and electrochemical analyses revealed that the electronic structure of 2 is typical of low-symmetrically benzene-fused phthalocyanines,⁶ whereas **3** exhibits a rather tetraazachlorine-like electronic structure⁷ due to an unusual twist of the structure at the sevenmembered ring unit. Among these core-modified phthalocyanine analogues, the unique electronic structure of 3 has motivated us to change the external ring unit from a biphenyl unit to a phenanthrene unit or a bipyridine unit by using 4,5-phenanthrenedicarbonitrile 4 or 2,2'-bipyridyl-3,3'-dicarbonitrile 5 in order to obtain insight into the effects of peripheral conjugation or external coordination on the electronic structures of **3**.

4,5-Phenanthrenedicarbonitrile **4** and 2,2'-bipyridyl-3,3'-dicarbonitrile 5 were synthesized according to the literature procedures.^{8,9} Mixed-condensation reactions of these nitriles with 4,5-di-p-tert-butylphenyloxyphthalonitrile in the presence of nickel acetate and ammonium molybdate in quinoline at 330 °C provided core-modified analogues with a seven-membered ring unit (7 and 8) in 1.7% and 2.1% yields, respectively, together with phthalocyanine 6 (Scheme 1).^{10,11} The HR-ESI-MS exhibits molecular ion peaks and theoretical distribution patterns corresponding to the structures of **7** and **8** (**7**: m/z = 1559.6566, calcd for $C_{100}H_{93}N_8NiO_6 = 1559.6572 [M^++H], 8: m/z = 1559.6290, calcd for$ $C_{96}H_{90}N_{10}NiO_6Na = 1559.6296 [M^++Na]$). The ¹H NMR spectrum of **7** in CD₂Cl₂ exhibits α -benzo proton peaks as a singlet at 8.45, 8.38, and 8.06 ppm and phenanthrene proton peaks at 8.01 (doublet), 7.90 (singlet), 7.58 (triplet), and 6.84 (doublet) ppm. This peak pattern reflects a twofold molecular symmetry of 7. A similar twofold molecular symmetry of **8** was also inferred from the ¹H NMR spectrum of **8** in CD_2Cl_2 , which exhibits three α -benzo protons peaks at 8.37, 8.09, and 7.98 ppm and three bipyridyl proton



Chart 1. Phthalocyanine and core-modified phthalocyanine analogues.





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Scheme 1. Syntheses of phthalocyanine analogues bearing a seven-membered ring unit (7 and 8).

peaks at 8.83 and 7.22 ppm with the integration ratio of 1:2. The significant up-field shift of the 3- and 6-phenanthrene protons and the 4- and 4'-bipyridyl protons from the corresponding proton peaks of **4** and **5** is indicative of twisted conformations for **7** and **8**, in which hydrogen atoms at these positions lie above and below the macrocyclic 18π -conjugation systems.

Compounds **7** and **8** exhibit similar split Q bands in the longer and shorter wavelength regions compared to the single Q band of phthalocyanine **6** at 675 nm (791 and 618 nm for **7** and 791 and 624 nm for **8**, Fig. 1). The shapes of these absorption spectra are also similar to that of **3**.⁵ Corresponding to the split Q bands, Faraday *B* terms at 819 (minus) and 619 (plus) nm for **7** and at 820 (minus) and 624 (plus) nm for **8** are observed in the magnetic circular dichroism (MCD) spectra, which is indicative of the presence of non-degenerate excited states of **7** and **8** and a larger energy difference of the frontier HOMOs than that of the frontier LUMOs.¹² These electronic absorption and MCD spectral features suggest tetrazachlorine-like electronic structures for **7** and **8**.⁷

The cyclic voltammograms reveal one reversible oxidation at 0.08 V for **7** and 0.27 V for **8** (vs Fc⁺/Fc) and two reversible reductions at -1.40 V and -1.78 V for **7** and at -1.25 V and -1.65 V



Figure 1. Absorption (bottom) and MCD (top) spectra of 7 (black line) and 8 (blue line) in CHCl₃.

for **8**. Similar potential differences between the first oxidation and reduction (1.48 V for **7** and 1.52 V for **8**) are consistent with the similar Q band energies of these compounds. The negative shifts of the redox potentials of **7** from those of $\mathbf{3}^5$ and **8** can be interpreted in terms of destabilization of both the HOMO and LUMO of **7** upon fusion of a benzene ring to the structure of **3**.

Optimized structures of 7 and 8 based on DFT calculations at B3LYP/6-31G(d) level exhibit significant twist of these molecules at the seven-membered ring units, which is in good agreement with the proposed conformations from the NMR measurements. Dihedral angles between the phenanthrene and bipyridyl moieties from the rest of the molecules are 72° and 77°, respectively, whereas the torsion angles of these moieties are 18° for 7 and 37° for 8 (Fig. 2). Almost perpendicular orientation of the sevenmembered ring units in 7 and 8 can rationalize very small MO coefficients at the seven-membered ring units in the frontier orbitals (Fig. 3), which can also be observed in the case of **3**.⁵ The slightly higher energies of the frontier MOs in 7 compared to those of 3 and 8 well reproduce the observed negative shift of the redox potentials of this compound in the cyclic voltammetry measurements. As a result of the lowering of the molecular symmetry and changes in the main conjugation pathway from phthalocyanines, both compounds exhibit a large energy difference between the LUMO and LUMO+1. Time-dependent (TD) DFT calculations on **7** and **8** at B3LYP/6–31G(d) level, thus, predict split theoretical Q bands comprising transitions from the HOMO to the LUMO and the LUMO+1 at 698 and 594 nm for 7 and at 700 and 597 nm for 8 (Table 1). These theoretical absorption spectra are in good agreement with the observed electronic absorption and MCD spectra.

The peripheral bipyridyl moiety in **8** can be used as an outer coordination site for transition metals to provide metal-linked dimer or trimer systems.¹³ A preliminary study using a ruthenium



Figure 2. Optimized structures of 7 (left) and 8 (right) (B3LYP/6-31G(d)).



Figure 3. Partial molecular orbital diagrams of 7 (left) and 8 (right) (B3LYP/6-31G(d) level).

Table 1 Selected transition energies and wave functions of ${\bf 7}$ and ${\bf 8}$ based on the TDDFT method (B3LYP/6–31G(d))

Compd	Energy (nm)	f ^a	Wave function ^b
7	698 594	0.32 0.24	$\begin{array}{c} +0.594 173 \leftarrow 172 > +0.122 174 \leftarrow 166 > + \dots \\ +0.583 174 \leftarrow 172 > -0.122 173 \leftarrow 166 > \\ +0.142 175 \leftarrow 172 > +0.110 177 \leftarrow 172 > +\dots \\ +0.593 172 - 172 > +0.110 177 \leftarrow 172 > +\dots \\ +0.593 174 - 172 > +0.110 177 - 172 > +\dots \\ +0.593 174 - 172 > +0.110 177 - 172 > +\dots \\ +0.593 174 - 172 - 172 > +\dots \\ +0.593 174 - 172 - 172 > +\dots \\ +0.593 174 - 172 - 172 - 172 > +\dots \\ +0.593 174 - 172 - $
8	700 597	0.32 0.24	+0.593 167 \leftarrow 166> +0.105 168 \leftarrow 161> + +0.588 168 \leftarrow 166> +0.105 169 \leftarrow 165> +0.172 169 \leftarrow 166> +

^a Oscillator strength.

^b Wave functions based on the eigenvectors predicted by TDDFT. The |172> and |166> represent the HOMO of **7** and **8**, respectively. Eigenvectors greater than 0.10 are included.

ion has revealed the formation of a trimer system based on MALDI-TOF-MS. Although coordination of the ruthenium ion reduces the torsion angle of the bipyridyl moiety, significant changes in the absorption spectra were not observed (see Supplementary data), which can be rationalized from the fact that **7** and **8**, which have different torsion angles, still exhibit similar spectral features.

In summary, two novel core-modified phthalocyanine analogues with a seven-membered ring unit were successfully synthesized from aromatic dicarbonitriles bearing cyano groups at 1, 4-separate positions. In spite of the difference in the peripheral ring units and the torsion angles of these moieties, all the compounds exhibit similar spectral and electrochemical features stemming from their tetraazachlorine-like electronic structures. The peripheral coordination site of **8** can potentially be used to construct coordination oligomers without changing the spectroscopic properties, and research along this direction is currently being investigated.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.11.092.

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- Selected data for 8: ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ = 8.83 (br s, 2H; pyridyl), 8.37 (s, 2H; α-benzo), 8.09 (s, 2H; α-benzo), 7.98 (s, 2H; α-benzo), 7.36 (d, J = 8.4 Hz, 4H; phenyloxy), 7.31 (m, 8H; phenyloxy), 7.22 (m, 4H; pyridyl), 7.10 (d, J = 8.4 Hz, 4H; phenyloxy), 7.06 (d, J = 9.0 Hz, 4H; phenyloxy), 6.88 (d, J = 7.8 Hz, 4H; phenyloxy), 1.33 (s, 18H; t-butyl), 1.31 (s, 18H; t-butyl), and 1.28 ppm (s, 18H; t-butyl); UV/vis (CHCl₃): λ_{max} [m] (ε) = 354 (37000), 623 (41000), and 791 (51000 M⁻¹ cm⁻¹); HR-ESI-TOF-MS: m/z (%): 1559.6290 (100); Calcd for C₉₆H₉₀₀N₁₀O₆NiNa [M*+Na]; 1559.6296.
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