

Synthesis and Electronic Properties of an Azulene-fused Tribenzotetraazaporphyrin

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A novel tribenzotetraazaporphyrin with a fused azulene ring was synthesized via mixed condensation reaction of 5,6-dicyanoazulene and 3,6-dibutoxyphthalonitrile. The macrocycle exhibited several intense absorption peaks from 600 to 900 nm. The spectroscopic properties were analyzed by DFT calculations.

Much effort has been made to develop various types of near-infrared organic compounds because of their potential applications in organic solar cells, photodynamic therapy for cancer, heat absorbers, and near-infrared imaging.¹ Since most near-infrared dyes are unstable, breakthroughs in molecular design and synthetic strategy to develop superior dyes are required by the scientific community. Phthalocyanine derivatives such as naphthalocyanines are typical near-infrared dyes in terms of their intense absorption in the Q band region.² Recently, our group has reported a new class of near-infrared phthalocyanine derivatives in which four azulene units were fused to a tetraazaporphyrin skeleton.³ The azulene-fused macrocycle **1** (Chart 1), which is referred to as azulenocyanine, can be regarded as a structural isomer of naphthalocyanines. It was revealed that expanding a tetraazaporphyrin π -system by fusion with four azulene units drastically lowered the LUMO level of the macrocycle. Herein we report the synthesis, spectroscopic properties, and theoretical calculations of a new unsymmetrically substituted phthalocyanine derivative **2** in which one fused benzene ring was replaced by an azulene ring. The results were compared to those of the corresponding phthalocyanine **3** to enhance our understanding of spectral changes by extended π -conjugation with azulene.

The azulene-fused macrocycle **2** was prepared by a cross-cyclotetramerization reaction. A mixture of 5,6-dicyanoazulene³ (53.5 mg, 0.30 mmol), 3,6-dibutoxyphthalonitrile (245 mg, 0.90 mmol), nickel(II) chloride (194 mg, 1.50 mmol), urea (288 mg, 4.80 mmol), and ammonium molybdate (12.0 mg, 0.01 mmol) in dry quinoline (3.0 mL) was stirred at 180 °C under argon atmosphere for 22 h. After the mixture was cooled to room

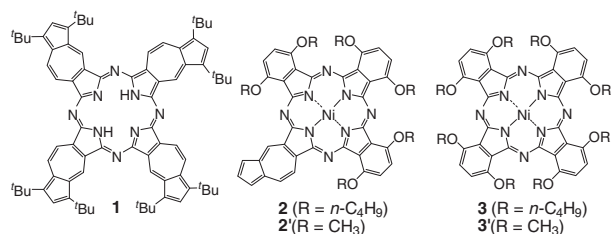


Chart 1.

temperature, the reaction mixture was poured into methanol and filtrated. After the filtrate was dissolved in CHCl_3 , purification by silica gel column chromatography and size-exclusion column chromatography (Bio-beads S-X1, Bio-Rad Laboratories Inc.) using CHCl_3 furnished the desired compound as a deep-green solid (2.6 mg, 1%). Structural determination of **2** was based on ¹HNMR, HRMS, and electronic absorption spectroscopy.⁴

Figure 1 shows the ¹HNMR spectrum of **2**. The chemical shifts of azulene protons near the tetraazaporphyrin skeleton (H_a and H_b) exhibited down-field shifts, which can be interpreted in terms of the strong ring current of the macrocycle. The extent of the shifts is similar to that of the azulenocyanine (**1**).³

Figure 2a shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **2** in CHCl_3 , together with those of 1,4,8,11,15,18,22,25-octabutoxyphthalocyaninato-nickel(II) (**3**) as a reference. A single Q band was observed at 745 nm for the symmetric phthalocyanine **3**.⁵ In the case of the azulene-fused macrocycle, several intense absorption peaks (746, 816, and 864 nm) were observed in the near-infrared region. Since spectral red shift of naphthalene-fused tribenzotetraazaporphyrins is much smaller than that of **2**,⁶ it is confirmed that the azulene unit impacts profoundly the optical properties of the tetraazaporphyrin, compared with a naphthalene unit.

The MCD signal pattern of **2** is characteristic of this class of low-symmetry phthalocyanine derivatives.⁷ Thus, the Q band peak positions in the MCD spectrum were nearly identical to those in the absorption spectrum, which is in contrast to the intense derivative-shaped MCD signal of **3**. This indicates that compound **2** has split Q absorption bands.

In order to deepen our interpretation of the spectra of the azulene-fused tetraazaporphyrin, DFT calculations were carried

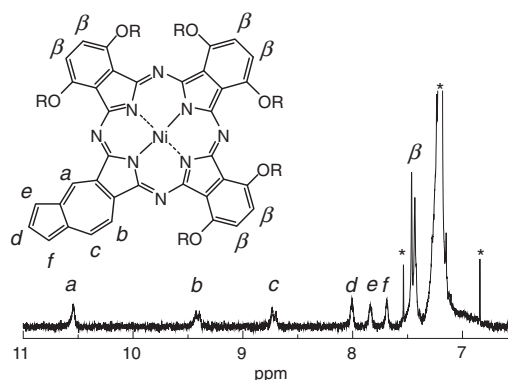


Figure 1. Partial ¹HNMR spectrum of **2** in CDCl_3 . Asterisks indicate solvent peaks.

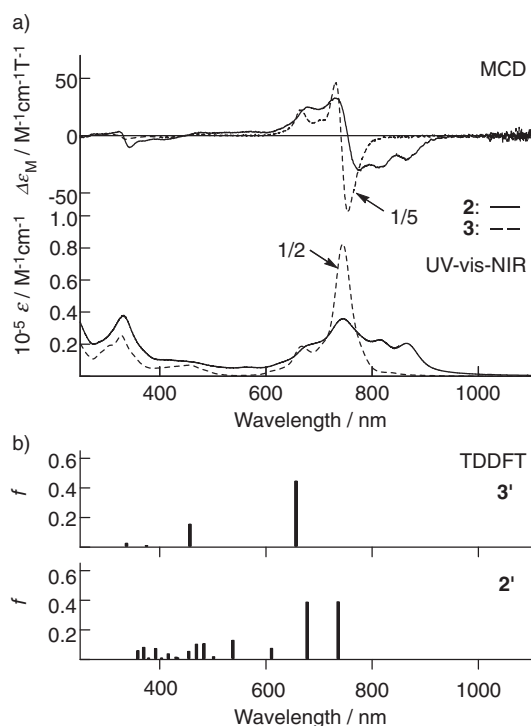


Figure 2. a) MCD and electronic absorption spectra of **2** (solid line) and **3** (broken line) measured in $CHCl_3$. b) Calculated absorption stick spectra of **2'** and **3'** (B3LYP/6-31G*).

out. Thirty excitation energies and oscillator strengths for the optimized structures of model compounds **2'** and **3'** were obtained using the TDDFT method (Figure 2b).⁸ The calculated spectral features appear to be in fairly good agreement with the observed spectra. A degenerate transition calculated at 658 nm for the model phthalocyanine **3'** was split into two transitions (737 and 678 nm) for the azulene-substituted molecule **2'**. Polarization of the two transitions was almost perpendicular to each other. From these results, the absorption bands observed at 746 and 864 nm can be assigned to two split Q transitions. The absorption band at 816 nm is probably due to a vibronic band.

Energy levels of frontier molecular orbitals and their contour plots of the model compounds are shown in Figure 3. The HOMO–LUMO gap of the phthalocyanine was 2.04 eV, while the HOMO–LUMO and HOMO–LUMO+1 gap of **2'** were calculated to be 1.85 and 2.00 eV, respectively. This means that the HOMO–LUMO gap of the azulene-fused macrocycle decreases because of the lowering of the LUMO level.

Cyclic voltammetry was carried out on the azulene-fused macrocycle **2** and the reference phthalocyanine **3** in CH_2Cl_2 with 0.1 M $n-Bu_4NClO_4$. As shown in Figure 4, the azulene-fused compound **2** exhibited two one-electron reversible reduction waves and a one-electron quasireversible oxidation wave. The first oxidation potential ($E_{ox,1}$) and the first reduction potential ($E_{red,1}$) of **2** were estimated to be +0.02 and −1.26 V (vs. Fc^+/Fc), while $E_{ox,1}$ and $E_{red,1}$ of **3** were +0.02 and 1.43 V. The separation of $E_{ox,1}$ and $E_{red,1}$ was decreased for **2** (1.28 V) relative to **3** (1.45 V). The observed electrochemical data correlate well with the DFT calculations.

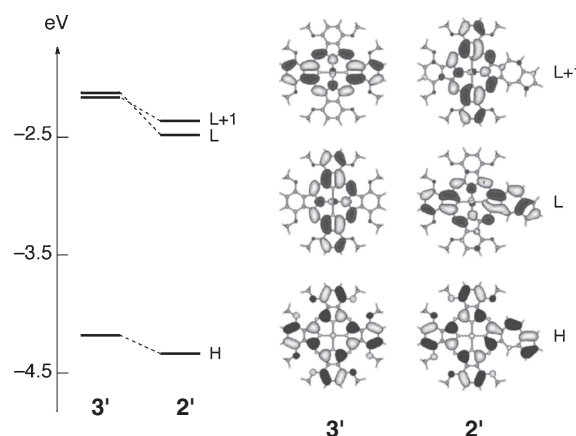


Figure 3. Energy levels of frontier molecular orbitals and their contour plots obtained from the B3LYP/6-31G* calculations. H = HOMO, L = LUMO. The LUMO of **3'** is doubly degenerate.

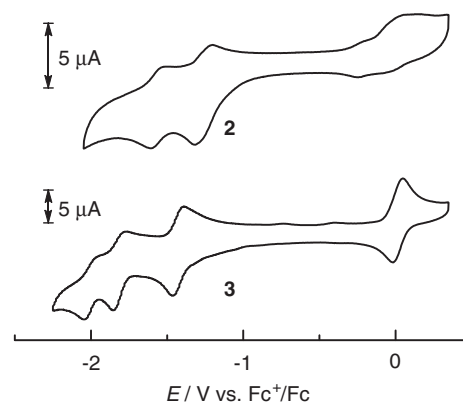


Figure 4. Cyclic voltammograms of **2** (top) and **3** (bottom) in CH_2Cl_2 with 0.1 M $n-Bu_4NClO_4$. The data were obtained using a glassy-carbon working electrode and Ag/AgCl reference electrode at a scan rate of 100 mV s^{−1}.

In summary, we have synthesized Ni(II) azulenotribenzotetraazaporphyrinatonicel(II) **2** to investigate the effect of the azulene unit in the tetraazaporphyrin skeleton. The azulene-fused macrocycle exhibited a broad absorption band in the near-infrared region. The molecular design is expected to be applicable to synthesize a range of novel near-infrared absorbing organic materials.

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 - 4 Selected data of compound **2**: ^1H NMR (300 MHz, CDCl_3): δ 10.61 (1H, brs), 9.48 (1H, d), 8.78 (1H, d), 8.08 (1H, brs), 7.91 (1H, brs), 7.76 (1H, brs), 7.6–7.4 (6H, brs), 4.9–4.7 (8H, m), 4.7–4.6 (4H, m), 2.3–1.9 (12H, m), 1.7–1.5 (12H, m), 1.09 (12H, t, $J = 7.2$ Hz), 0.88 (6H, t, $J = 7.2$ Hz). UV–vis (CHCl_3): λ_{max} ($\varepsilon \times 10^{-4}$) = 864 (2.0), 816 (2.3), 746 (3.6), 331 (3.8) nm. HRMS (FAB) m/z : (M^+) calcd for $\text{C}_{60}\text{H}_{66}\text{N}_8\text{NiO}_6$, 1052.4459; found, 1052.4491.
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 - 8 Ground state geometries of the model compounds were calculated at the level of B3LYP/6-31G*, using C_s (**2'**) and D_{4h} (**3'**) symmetry restriction.