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Azulenocyanine: A New Family of Phthalocyanines with Intense Near-IR Absorption

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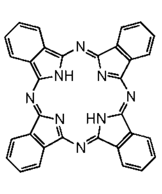
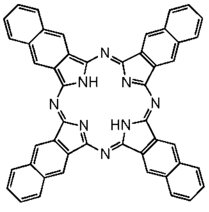
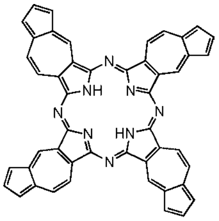
Near-IR dyes are required for various advanced technologies, including organic solar cells,[1] photodynamic therapy for cancer,[2] and near-IR imaging.[3] Phthalocyanine (Pc) derivatives, such as naphthalocyanines (Ncs), are a particularly important group of near-IR absorbing organic compounds, because they are more stable to heat and light than other types of organic dyes.[4]



phthalocyanine (Pc)



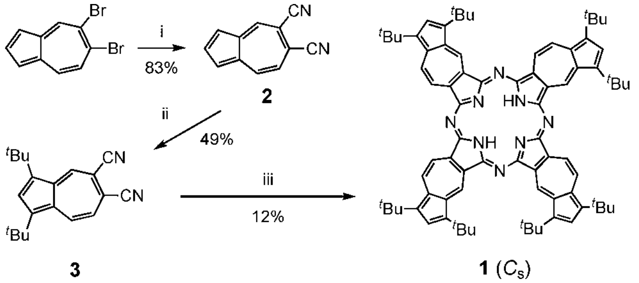
naphthalocyanine (Nc)



azulenocyanine

Ncs were first synthesized by de Diesbach et al. in 1927.[5] Although various types of Nc derivatives have been studied, their structural isomer, azulene-fused tetraazaporphyrin, has not been synthesized. We call this type of macrocycle *azulenocyanine* as a conventional name. Since the electronic properties of azulene are significantly different from those of naphthalene, extended π-conjugation with azulene is expected to have a marked effect on the optical properties. In the case of porphyrin systems, the azulene unit has an important influence on the electronic structure.[6] We herein report synthesis, unique spectroscopic properties, and theoretical calculations of the first example of an azulenocyanine, in which four azulene rings are connected at the 5- and 6-positions. The fused azulene units are expected to lower the LUMO level of the macrocycle, due to the electron-accepting nature of the seven-membered azulene skeleton.

Scheme 1. Synthesis of Azulenocyanine (**1**)[a]



[a] (i) CuCN (3.0 equiv), DMF, reflux, 17 h. (ii) ^{t}BuCl (6.0 equiv), $AlCl_3$ (3.0 equiv), CH_3NO_2, rt, 6 h. (iii) Li (6.0 equiv), *n*-hexanol, reflux, 4 h.

Octa-*tert*-butyl 5,6-azulenocyanine (**1**) was successfully synthesized via a multistep procedure (Scheme 1). We first prepared 5,6-dicyanoazulene (**2**) from 5,6-dibromoazulene[7] by use of the Rosenmund−von Braun reaction.[8] When a condensation reaction of **2** was conducted using *n*-hexOLi or zinc acetate as a template, an insoluble black powder was obtained. Although the desired molecular ion at $m/z = 776.1$ (calculated for $C_{48}H_{24}N_8Zn$ m/z 776.1415) was detected by MALDI-TOF-MS, the product could not be fully characterized due to its poor solubility in all organic solvents examined. With the aim of improving the solubility, 1,3-di-*tert*-butyl 5,6-dicyanoazulene (**3**) was synthesized by means of Friedel−Crafts alkylation of **2**.[9] The structure of **3** was confirmed by NMR and X-ray diffraction analysis (see Supporting Information).

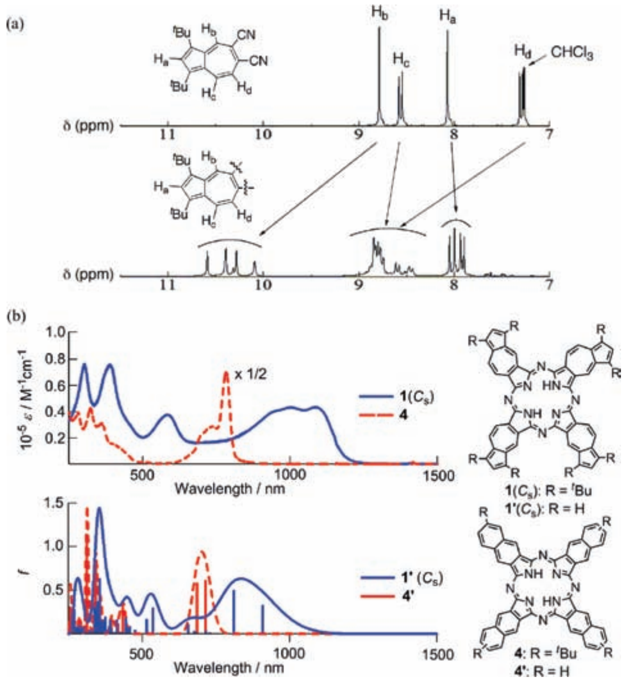


Figure 1. (a) ^{1}H NMR spectra of **3** (in $CDCl_3$ at 298 K, top) and **1** (in 1,4-dioxane-d_8 at 353 K, bottom). (b) Electronic absorption spectra of the C_s isomer of **1** (blue, solid line) and **4** (red, broken line) measured in $CHCl_3$. Calculated absorption spectra (B3LYP/6-31G*) are shown at the bottom. Gaussian bands with half-bandwidth of 1000 cm^{-1} (**4′**) or 2000 cm^{-1} (**1′**) were used.

The metal-free azulenocyanine (**1**) was obtained as a mixture of structural isomers by cyclic tetramerization of **3** in the presence of *n*-hexOLi. The product showed the parent-ion peak at m/z = 1162.7299 (calculated for $C_{80}H_{90}N_8$ m/z 1162.7288) in high-resolution ESI-TOF-MS. The major isomer with C_s symmetry was isolated by means of HPLC.[10] Figure 1a shows the ^{1}H NMR spectra of the precursor **3** and the C_s isomer of **1**. The chemical shifts of hydrogens near the tetraazaporphyrin skeleton of **1** (H_b and H_d) were at lower field compared with those of **3**, indicating that a strong diatropic ring current is present in **1**, as is the case with regular

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phthalocyanines. The *tert*-butylated azulenocyanine obtained is soluble in common organic solvents, such as toluene, chloroform, and THF.

Figure 1b shows the electronic absorption spectrum of **1** (C_s). Interestingly, the azulenocyanine (**1**) exhibits a broad absorption spectrum which covers the whole visible and near-IR regions, far beyond 1000 nm. The lowest-energy absorption band was observed at 1085 nm, and its extinction coefficient was 4.3×10^4 M^{-1} cm^{-1}. These spectral features are completely different from those of metal-free tetra-*tert*-butyl 2,3-Nc (**4**) and the azulene precursor **3**. The λ_{max} of **1** is much longer than that of anthracene-fused tetraazaporphyrin (anthracocyanine, $\lambda_{max} = 831.5$ nm).[11] Although the metal-free anthracocyanine decomposes within a few days, the azulenocyanine (**1**) is stable under ambient conditions.

TDDFT calculations reproduced well the spectral differences between **1** and **4**. The near-IR absorption bands observed for the azulenocyanine can be assigned to the HOMO→LUMO and HOMO→LUMO+1 transitions (Q transitions) of the macrocycle. This assignment was supported by intensely coupled Faraday *B* terms in the magnetic circular dichroism (MCD) spectrum of **1** (see Supporting Information).[12]

The origin of the spectral features of **1** can be rationalized by means of MO analysis. Figure 2 shows frontier orbitals of Pc, Nc (**4′**), and **1′** (C_s). In the case of Nc, the HOMO−LUMO gap is decreased mainly due to destabilization of the HOMO level. In contrast, the LUMO energy of the azulenocyanine **1′** is significantly lowered, while the destabilization of the HOMO is modest. This leads to a smaller HOMO−LUMO gap (1.50 eV) than that of Nc (1.79 eV).

Cyclic voltammetry measurements were used to study the redox behavior of the C_s isomer of **1** in CH_2Cl_2 solution (see Supporting Information). The first oxidation potential ($E_{ox,1}$) and the first reduction potential ($E_{red,1}$) were +0.39 and −0.62 V (vs Ag/AgCl). Since the potentials for tetra-*tert*-butyl 2,3-Nc (**4**) are +0.54 and −0.92 V,[13] the shift in $E_{red,1}$ is larger than that in $E_{ox,1}$. The separation of $E_{ox,1}$ and $E_{red,1}$ was decreased for **1** (1.01 V) relative to **4** (1.46 V). These electrochemical data correlate well with the above calculation results.

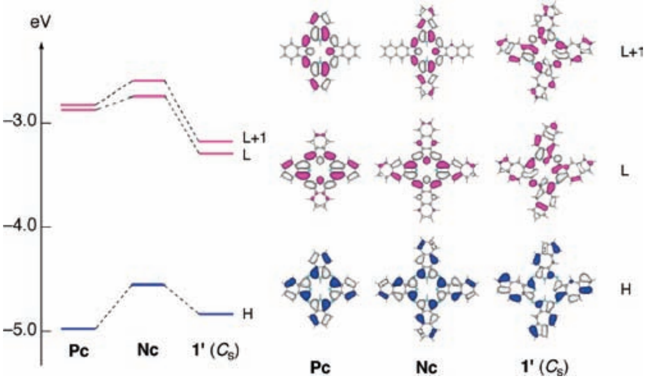

Figure 2. Energy levels of frontier molecular orbitals and their contour plots obtained from B3LYP/6-31G* calculations. H = HOMO, L = LUMO.

In conclusion, a convenient methodology has been developed to synthesize the first example of azulenocyanines. The azulene−tetraazaporphyrin conjugate has near-IR absorptions, high extinction coefficients, and a small HOMO−LUMO gap. The azulene unit significantly lowers the LUMO level of the macrocycle, while destabilization of the HOMO level is modest. This implies that the combination of azulene π systems with a tetraazaporphyrin skeleton can be exploited to design a new type of near-IR absorbing dyes with high stability against oxidation. The application of azulenocyanines to organic solar cells and near-IR imaging is currently being examined.

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Supporting Information Available: Experimental procedures, spectral data, crystallographic data for **4**, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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