Porphyrinoids

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A Quadruply Azulene-Fused Porphyrin with Intense Near-IR Absorption and a Large Two-Photon Absorption Cross Section**

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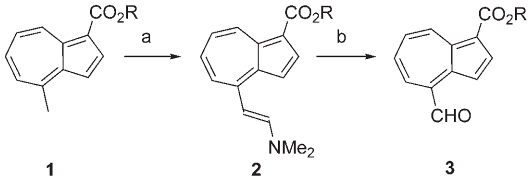
Considerable efforts have been continuously devoted to the exploration of extensively π-conjugated porphyrins in light of their potential applications in optoelectronic devices, sensors, photovoltaic devices, and so forth.[1–3] Recently, some of these conjugated porphyrins have been shown to exhibit large two-photon absorption (TPA) cross sections as a promising attribute.[4] The great promise of conjugated porphyrins relies on their flexible electronic systems, which are susceptible to peripheral modifications. An effective synthetic strategy is to fuse an aromatic segment directly onto the periphery of the porphyrin unit to expand a conjugated electronic system that is forced to take a planar conformation favorable for π conjugation.[5] Among such aromatic-fused porphyrins, Scott and co-workers reported an *anti*-bisnaphthoazulene-8-one-fused–Cu^{II} porphyrin that exhibited a Q-band-like absorption band at 1204 nm and a very small electrochemical HOMO–LUMO gap (1.17 V) as the most π-expanded example of a monomeric porphyrin.[5d] In this fusion strategy, azulene may be an effective aromatic segment because of the unique dipolar and polarizable electronic property that arises from its nonalternant hydrocarbon nature.[6] Previously, we prepared a series of directly linked *meso*-azulenylporphyrins, except for one bearing a 4-azulenyl group, and found that 1- and 6-azulenyl groups actually served as electron-donating and electron-withdrawing substituents, respectively, toward a Zn^{II} porphyrin, but the influence of such singly linked azulenyl groups upon the electronic system of the porphyrin are only small.[7]

Herein, we employed 4-azulenylporphyrin as a precursor of azulene-fused porphyrin targets, as the electron-rich 3-position of the azulene, which is directed toward the porphyrin, may be used for an oxidative ring-closing reaction. It has been reported that 1-methoxycarbonyl-4-formylazulene (**3a**) was prepared from 1-methoxycarbonyl-4-methylazulene (**1a**) by selective dibromination at the 4-methyl group followed by oxidation,[8] but treatment of **1a** with *N*-bromosuccinimide (NBS) led to predominant bromination at the 3-position in our hands. Therefore, aldehyde **3a** was prepared via enamine **2a** from **1a**.[9] Treatment of **1a** with *N*,*N*-dimethylformamide (DMF) dimethylacetal in DMF at 140 °C gave **2a**, which was oxidized to **3a** with $NaIO_4$ in 81 % yield in two steps. Dipyrromethane **4a** was prepared by the condensation reaction of **3a** with excess pyrrole in 94 % yield (Scheme 1).



Scheme 1. Synthesis of **3** (R = Me (**a**), octyl (**b**), 2,4,6-tri-*tert*-butylphenyl (**c**)). a) $Me_2NCH(OMe)_2$, DMF, 140 °C; b) $NaIO_4$, THF/H_2O.

Ni^{II}–5-(4-azulenyl)porphyrin **6** was prepared from the cross-condensation of dipyrromethanes **4a** and **5** with 3,5-di(*tert*-butyl)benzaldehyde followed by Ni^{II}-ion insertion in 16 % yield, and Ni^{II}–5,15-bis(4-azulenyl)porphyrin **7** was prepared from **4a** and 3,5-di(*tert*-butyl)benzaldehyde in 16 % yield. ^{1}H NMR spectrum of **7** displays two sets of signals in a 1:1 ratio, thus indicating the presence of two atropisomers. Ni^{II}–5,10,15,20-tetrakis(4-azulenyl)porphyrin

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8a was prepared from **3a** under Lindsey conditions[10] in 12% yield as a mixture of atropisomers. Structural determination of these azulenylporphyrins were mainly based on ^{1}H NMR spectroscopic, MALDI-TOF mass-spectrometric, and UV/Vis absorption spectroscopic analysis. The structure of the Cu^{II} complex of **6** [Cu(**6**)] was confirmed by X-ray diffraction analysis (Figure 1),[11] which showed that the 4-azulenyl group is linked to the porphyrin ring with a C–C bond length of 1.505 Å and a dihedral angle of 81°, similar to other *meso*-azulenylporphyrins.[7]

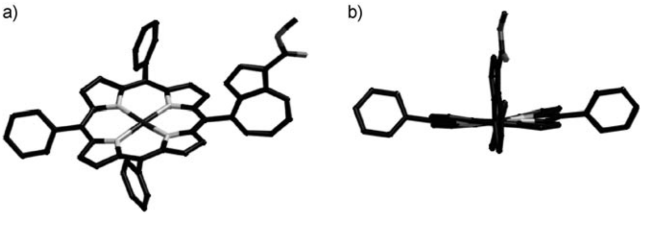
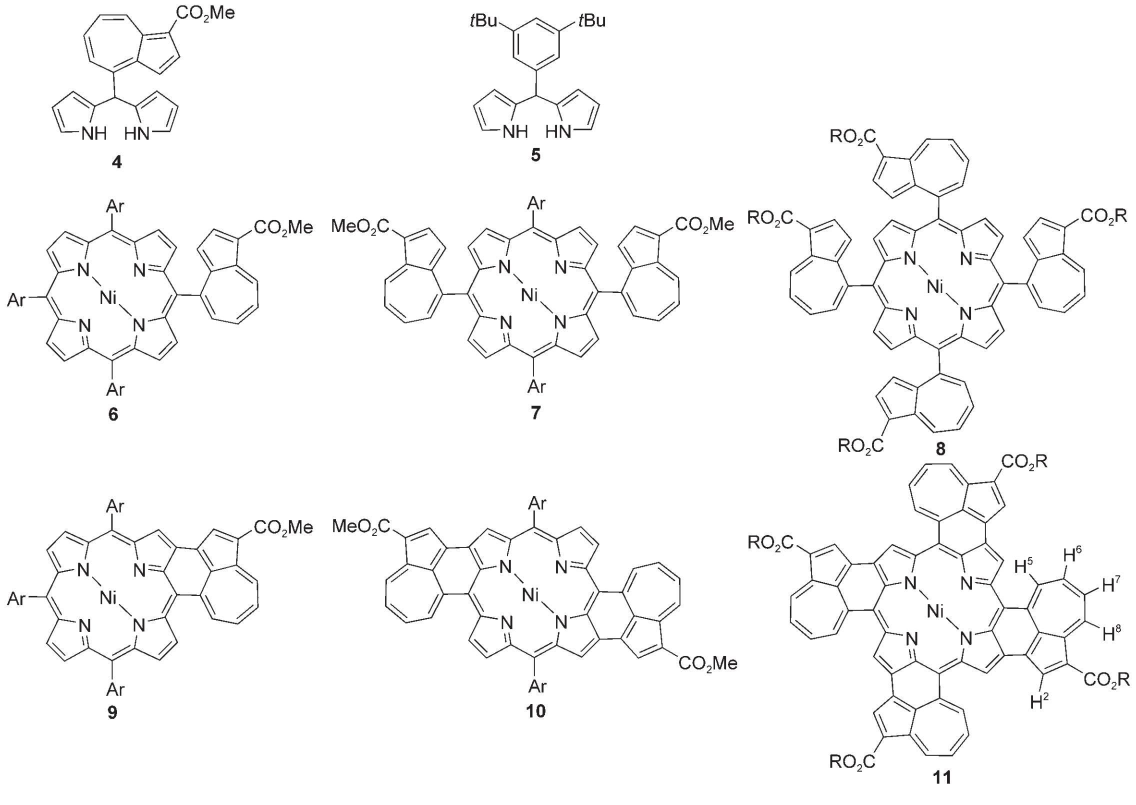


Figure 1. X-ray crystal structure of [Cu(**6**)]. a) Oblique view, b) side view. The *tert*-butyl groups and hydrogen atoms have been omitted for clarity.

Attempted oxidative ring-closing reaction of **6** with $AgPF_6$[12] did not cause any conversion, but the use of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)/[Sc(OTf)$_3$][2d] (Tf = trifluoromethanesulfonyl) as a stronger oxidant gave rise to a complicated mixture. In the meantime, we found that treatment of **6** with $FeCl_3$[13] under mild conditions (5 min, room temperature) afforded azulene-fused porphyrin **9** in 63% yield. A double ring-closing reaction of **7** was performed under similar conditions to regioselectively provide only the *anti* isomer **10** in 84% yield. Curiously, the *syn* isomer was not detected at all. This result suggested that the regiochemistry of the second ring-closing reaction is strongly influenced by the preformed azulene-fused structure at the opposite side. The symmetric *anti* structure of **10** is indicated by its simple ^{1}H NMR spectrum, which exhibits a single set of signals for the *meso* aryl protons, *para* protons ($\delta = 7.83$ ppm), and *ortho* protons ($\delta = 7.91$ ppm). A fourfold ring-closing reaction of **8a** was attempted with $FeCl_3$ under similar conditions; however, a complicated mixture was yielded. Separation of this mixture turned out to be quite difficult as a result of its extremely low solubility. We thus changed substrates to more soluble porphyrins **8b** and **8c**,[14] which were prepared from **3b** and **3c**, respectively, through the same synthetic route used for **8a**. Although the similar treatment of **8b** with $FeCl_3$ also led to an intractable mixture of low solubility, porphyrin **8c** was cleanly transformed into quadruply azulene-fused porphyrin **11** as a major product in 60% yield. The product **11** showed its parent-ion peak at *m*/*z* 2017.0052, calculated for $C_{136}H_{140}N_4O_8Ni$ *m*/*z* 2017.0057 in the high-resolution electrospray ionization TOF mass spectrum. In line with the symmetric structure, the ^{1}H NMR spectrum of **11** was quite simple and featured a single set of signals for the azulene protons ($\delta = 8.74, 8.64, 8.45, 7.93$, and 9.89 ppm for H^2, H^5, H^6, H^7, and H^8, respectively; Scheme 2) and a singlet at $\delta = 9.12$ ppm for the pyrrolic β-protons. Furthermore, X-ray diffraction analysis confirmed the structure, in which the four azulene moieties are fused to the central porphyrin ring in a symmetric manner to constitute an overall coplanar structure, which exhibits strong ruffling with a mean deviation of 0.81 Å



Scheme 2. Compounds studied herein. R = Me (**8a**), octyl (**8b**), 2,4,6-*tert*-butylphenyl (**8c**, **11**).

with respect to the porphyrin macrocyclic plane of 24 atoms (Figure 2).[15] The Ni–N bond lengths are 1.863, 1.877, 1.893, and 1.894 Å between the Ni center and N(1)–N(4), respectively. The opposite halves are bent with 120.9 and 111.6° dihedral angles.

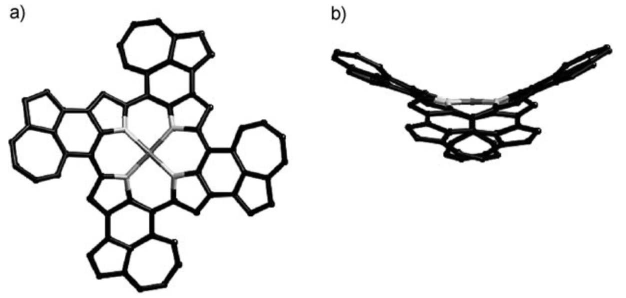


Figure 2. X-ray crystal structure of **11**. a) Top view, b) side view. The ester groups and hydrogen atoms have been omitted for clarity.

The absorption spectra of **6**–**8** exhibit slightly red-shifted, broadened Soret and Q bands. Such trends become larger upon an increase in the number of azulenyl groups; the Soret bands are observed at 422, 426, and 437 nm for **6**–**8**, respectively, and Q(1,0) bands are intensified in the order of **6** < **7** < **8** (Figure 3a). In sharp contrast, the azulene-fused structure causes more profound impacts in the electronic system of the porphyrin. The absorption spectrum of **9** shows a broad Soret band at 467 nm with a shoulder at 526 nm and a quite broad Q band that reaches around 1000 nm; the absorption spectrum of **10** shows a split Soret band at 487 and 545 nm and red-shifted, intense Q bands at 763, 898, and 1014 nm with roughly equal intensities; and the quardruply azulene-fused porphyrin **11** exhibits a drastically perturbed absorption spectrum with bands at 684 and 1136 nm, which cover the whole visible and near-IR regions up to approximately 1200 nm (Figure 3b). To the best of our knowledge, this large bathochromic shift is, as a monomeric porphyrin, comparable to the largest one reported by Scott and co-workers.[5d] Interestingly, the spectral shapes of the Q-band shape are considerably distorted for symmetry-broken fused porphyrins **9** and **10**, whereas that of the C_2-symmetric **11** restores a typical vibrational structure common to normal porphyrins.

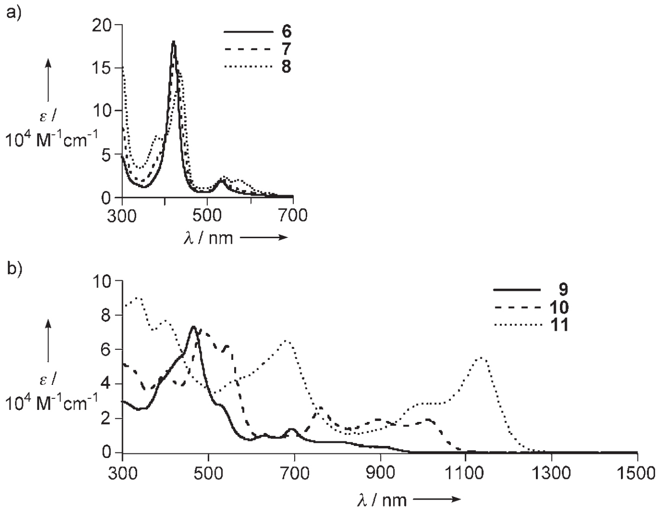


Figure 3. a) UV/Vis absorption spectra of **6**–**8**. b) UV/Vis–near IR absorption spectra of **9**–**11**.

As the very low-energy absorption band for **11** suggested a very small HOMO–LUMO gap, cyclic voltammetric studies were performed in benzonitrile (Table 1). The first oxidation potential ($E_{ox,1}$) and the first reduction potential ($E_{red,1}$) of **6** were positively shifted by introduction of an electron-withdrawing 4-azulenyl group relative to those of Ni^{II}–5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (Ni–TDBPP). The separation of $E_{ox,1}$ and $E_{red,1}$ was decreased dramatically for **9** (1.58 V) relative to **6** (2.27 V), and such a decrease was more significant for **10** (1.23 V) and **11** (1.01 V), thus reflecting the increased expanded π-electronic systems.

Table 1: Redox potentials in benzonitrile (versus ferrocene/ferrocenium; in V).

Compound	$E_{ox,1}$	$E_{ox,2}$	$E_{red,1}$	$E_{red,2}$	$E_{ox,1}-E_{red,1}$
6	0.65		−1.62		2.27
9	0.38	0.55	−1.20	−1.58	1.58
10	0.25	0.47	−0.98	−1.27	1.23
11	0.13	0.33	−0.88	−1.05	1.01
Ni–TDBPP	0.61		−1.73		2.34

We investigated the excited-state dynamics by transient absorption measurements (see the Supporting Information). The time-resolved spectroscopic investigations revealed that the photoexcited states of **9**–**11** decay biexponentially with fast decay components of 1–2-ps time constants and relatively slow components. The contribution of a long-lived (≈1.4 ns) component to the decay of photoexcited **11** is significant, thus indicating that the porphyrin $^1(\pi,\pi^*)$ state is largely responsible for the deactivation process. On the other hand, the photoexcited dynamics of **9** are very fast, mainly governed by an approximately 1-ps decay component. This feature is attributable to the decay of the (d,d) state, formed by unoccupied d orbitals of the central Ni^{II} in the porphyrin ring, as it has been well established that the (d,d) state acts as a quenching state in the energy relaxation dynamics of photoexcited Ni^{II} porphyrins.[16] The decay of photoexcited **10** shows an intermediate behavior between **9** and **11**, thus suggesting a competition between the $^1(\pi,\pi^*)$ and (d,d) states. In other words, while the low-lying (d,d) state remains at the relatively same energy, the position of the porphyrin-ring $^1(\pi,\pi^*)$ state in energy changes dramatically as the π-conjugation pathway increases from **9** to **11**.

The TPA cross-section values were measured by an open-aperture Z-scan method[17] with wavelength-tunable 130-fs pulses at a 5-kHz repetition rate generated from a femtosecond Ti:sapphire regenerative amplifier system. Pulses of sufficiently high power readily afford the power density enough for the TPA process without tight focusing, which eliminates unwanted nonlinear effects, such as self-focusing and white-light continuum generation. The maximum TPA cross section $\sigma^{(2)}$ values are 340 GM at 1200 nm for **1a**, 2050 GM at 1200 nm for **10**, and 7170 GM at 1380 nm for **11**, respectively. In addition, the TPA spectra of **11** in the 1300–1450-nm region indicate that two-photon allowed states should exist near 680–700 nm (see the Supporting Information). In the case of **11**, a highly notable enhancement of the $\sigma^{(2)}$ value in comparison with those of **9** and **10** demonstrates that the expansion of π conjugation by incorporating azulene-fused structures is the overriding factor in increasing the $\sigma^{(2)}$ value. The enlargement of azulene-fused structures gives rise to a very effective π-electron conjugation pathway throughout the porphyrin moiety.[4f]

In summary, the azulene-fused porphyrins, **9**, **10**, and **11** were synthesized through the oxidation of *meso*-(4-azulenyl)-porphyrins **6**, **7**, and **8c**, respectively, with $FeCl_3$. The azulene-fused strategy allowed the realization of highly π-conjugated porphyrinic electronic systems, which are promising TPA pigments.

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[11] Crystallographic data for [Cu(**6**)]: $C_{76}H_{81}Cl_6CuN_4O_2$, $M_r = 1358.69$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 19.2311(15)$, $b = 10.0770(8)$, $c = 36.129(3)$ Å, $b = 98.146(2)°$, $V = 6930.8(9)$ Å^3, $D_{calcd} = 1.302\ \mathrm{g\,cm^{-3}}$, $T = 90(2)$ K, crystal size $0.70 \times 0.40 \times 0.30\ \mathrm{mm^3}$, $R = 0.0996$ $(I > 2\sigma(I))$, $Rw = 0.2661$, GOF = 1.044. CCDC-600204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] The porphyrins **8b** and **8c** were prepared from **3b** and **3c** and pyrrole in 10 and 12 % yields, respectively, by using the methods developed by Lindsey.[10] The formylazulenes **3b** and **3c** were prepared by a similar route using **3a** (see the Supporting Information).

[15] Crystallographic data for **11**: $C_{136}H_{140}N_4NiO_8$, $M_r = 2017.23$, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 26.6423(14)$, $b = 42.798(2)$, $c = 26.3773(14)$ Å, $b = 104.820(2)°$, $V = 29076(3)$ Å^3, $D_{calcd} = 0.922\ \mathrm{g\,cm^{-3}}$, $T = 90(2)$ K, crystal size $0.55 \times 0.40 \times 0.35\ \mathrm{mm^3}$, $R = 0.0888$, $Rw = 0.2465$, GOF = 1.030. CCDC-600205 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Solvent molecules contained in the lattice were severely disordered and could not be resolved. The program SQUEEZE[18a] in PLATON[18b] was used to remove the solvent density.

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