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Communication

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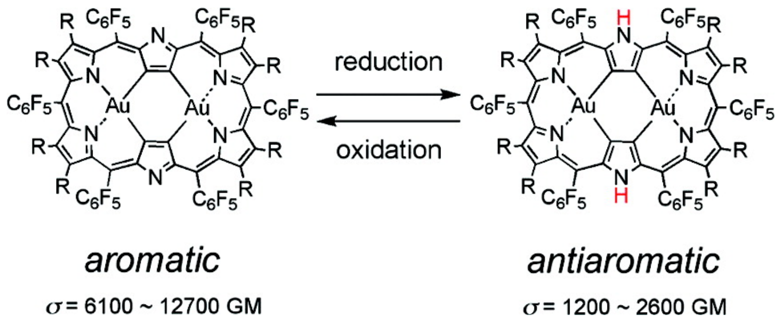

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Peripheral Fabrications of a Bis-Gold(III) Complex of [26]Hexaphyrin(1.1.1.1.1.1) and Aromatic versus Antiaromatic Effect on Two-Photon Absorption Cross Section

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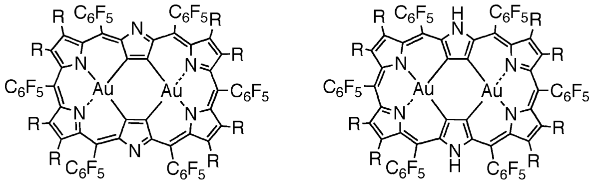
In recent years, there has been a growing interest in the development of organic molecules that have large two-photon absorption (TPA) cross-section values because of their potential applications in diverse fields including three-dimensional (3D) optical memory, deeper-penetrating photodynamic therapy, 3D microfabrication, and so on.[1] Design strategies toward the enhancement of TPA values have been explored mainly based on multichromophoric systems such as the incorporation of donor and acceptor groups in dipolar, quadrupolar, and octupolar molecular systems and the use of dendritic, multiply branched, three-dimensional, and coplanar systems.[2] Large TPA values are considered to arise from effectively delocalized conjugated networks, but understanding of structural and electronic factors that lead to large TPA still remains insufficient, requiring further systematic studies. In this respect, expanded porphyrins are particularly interesting and promising molecules due to their atom-economic large TPA values.[3−5] In order to enhance the TPA value of expanded porphyrins, peripheral substitution reactions will be useful but have not been available so far. Herein, we report the improved synthesis and peripheral modifications of [26]hexaphyrin bis-gold(III) complex **1** with the aim to enhance TPA value through expansion of the electronic network of expanded porphyrins. These reactions are of significant synthetic value since they can be performed in a designed manner similarly to those of porphyrins. These studies also allow us to examine the influence of aromatic-to-antiaromatic change upon TPA value as a rare case by taking advantage of rigid skeletons of hexaphyrin bis-gold(III) complexes, in which reversible interconversions between aromatic [26]hexaphyrin and antiaromatic [28]hexaphyrin bis-gold(III) complexes are feasible.[6]

Chart 1



1 R = H
3 R = Br
5 R = phenyl
7 R = phenylethynyl

2 R = H
4 R = Br
6 R = phenyl
8 R = phenylethynyl

Hexaphyrin bis-gold(III) complex **1** was prepared from [26]hexaphyrin(1.1.1.1.1.1)[7] by our reported metalation protocol.[6] Here, activation of $NaAuCl_4$ by the addition of Ag(I) salt improved the yield of **1** to 39%. For introduction of peripheral synthetic handles, we examined bromination of **1** with *N*-bromosuccinimide (NBS) under various conditions, which did not proceed at room temperature but under refluxing conditions provided mono-, di-, tri-, and tetrabrominated hexaphyrin bis-gold(III) complexes in low yields. These brominated products were difficult to separate due to their similar elution behaviors either on silica gel, alumina, or GPC column. After several experiments, we found that peripheral bromination proceeded slowly but steadily under harsh reaction conditions (reflux, in neat bromine, in the presence of Fe powder). After refluxing for 3 days and subsequent usual workup, octabrominated product **4** was isolated as a reduced 28π-form in a high yield (94%). Oxidation of **4** with MnO_2 proceeded smoothly for 30 min to furnish corresponding [26]hexaphyrin **3** quantitatively. The reduced form **4** is probably stabilized by the electron-deficient bromine substituents as judged from an observation that **3** was partially reduced during elution through a silica gel or alumina column. The successful bromination of **1** under the harsh conditions demonstrated its remarkable robustness.

Then, Suzuki−Miyaura coupling of **4** with phenylboronic acid was attempted in toluene in the presence of $Pd(PPh_3)_4$ and K_2CO_3 for 7 days, which provided a mixture of penta-, hexa-, hepta-, and octaphenylated products. Repeated separation by silica gel column chromatography using a 1:4 mixture of CH_2Cl_2 and hexane as an eluent and subsequent oxidation with DDQ gave **5** in 10% yield. Stille coupling of **4** with trimethyl(phenylethynyl)tin in the presence of $Pd(PPh_3)_4$ in THF for 24 h proceeded almost quantitatively, and subsequent simple separation over a short silica gel column gave octa-β-(phenylethynyl) hexaphyrin bis-gold(III) complex **7** in 90% yield. Complexes **5** and **7** were quantitatively reduced to antiaromatic [28]hexaphyrin bis-gold(III) complexes **6** and **8** with $NaBH_4$, respectively. All of these products were fully characterized by high-resolution mass spectroscopy and ^1H and ^{19}F NMR spectroscopy (Supporting Information, SI). In line with the previous study,[6] antiaromatic characters of **2**, **4**, **6**, and **8** are indicated by high-field shifted signals due to the outer NH protons appearing at 1.81, 1.06, 1.66, and 0.43 ppm, respectively.

The solid-state structures of **4**, **5**, and **7** (Figure 1) determined by single-crystal X-ray diffraction analysis revealed that the two Au(III) atoms are coordinated in the same NNCC pockets, keeping roughly planar but considerably bent structures with large mean plane deviations with respect to the macrocyclic 36 atoms; 0.666 Å for **4**, 0.516 Å for **5**, and 0.497 Å for **7**, which are larger than that of **1** (0.356 Å).[8] The large distortions may be ascribed to the steric congestion of the peripheral substituents. The Au−C and Au−N bond lengths are quite similar for the three complexes; 1.994(10)−2.000(9) and 2.069(8)−2.087(8) Å for **4**, 1.972(11)−1.991(13) and 2.072(11)−2.090(11) Å for **5**, and 1.995(8)−2.013(8) and 2.101(7)−2.111(7) Å for **7**. While the peripheral β-phenyl groups of **5** are attached to the hexaphyrin macrocycle with large dihedral angles of 53.6−89.0°, most of phenylethynyl groups in **7**

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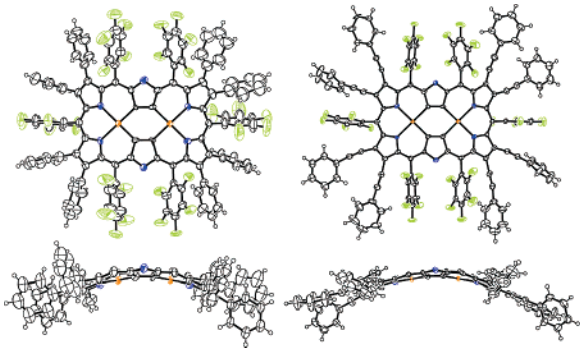

Figure 1. X-ray crystal structures of **5** (left) and **7** (right). The thermal ellipsoids are scaled to the 50% probability level. In the side views, *meso*-pentafluorophenyl substituents are omitted for clarity.

Table 1. TPA Values of **1**−**8**

	A/N[a]	λ (nm)[b]	σ (GM)	σ **(N)/**σ **(A)**
1	A	1260	6100 (±500)	−
2	N	1200	1200 (±300)	0.20
3	A	1380	8600 (±500)	−
4	N	1200	1600 (±500)	0.19
5	A	1380	7200 (±500)	−
6	N	1200	1700 (±500)	0.23
7	A	1410	12700 (±500)	−
8	N	1200	2600 (±500)	0.20

[a] A: aromatic, N: antiaromatic. [b] Excitation wavelength.

are roughly coplanar to the hexaphyrin core, apparently contributing to the extensive overall conjugation.

The absorption spectra of [26]- and [28]hexaphyrin bis-gold(III) complexes in CH_2Cl_2 are distinctly different, in that the former exhibit relatively sharp Soret-like bands around 700 nm along with four Q-band-like bands in the near-infrared region, but the latter do not display bands in the near-infrared region (SI). These spectral differences can be understood in terms of aromatic and antiaromatic characters for [26]- and [28]hexaphyrin bis-gold(III) complexes, respectively. The Soret-like bands are observed at 671 nm for **1**, 695 nm for **3**, 686 nm for **5**, and 715 nm for **7**. The absorption spectrum of **7** suggests effective conjugation of the hexaphyrin core with eight phenylethynyl groups. The spectral shapes are relatively similar among [28]hexaphyrin bis-gold(III) complexes, exhibiting highest peaks at 570 nm for **2**, at 587 nm for **4**, at 582 nm for **6**, and at 624 nm for **8** (SI).

The TPA cross-section values (σ) were measured by an open-aperture Z-scan method[9] with wavelength tunable 130 fs pulses at 5 kHz repetition rate generated from a femtosecond Ti:sapphire regenerative amplifier system at near-infrared wavelength so as to completely eliminate the contribution from one-photon absorption. As shown in Table 1, large TPA values were revealed for [26]-hexaphyrin bis-gold(III) complexes, probably reflecting effective electronic conjugation. These results are consistent with the structural features that the phenyl substituents in **5** are attached to the hexaphyrin macrocycle with large dihedral angles, but most of the phenylethynyl substituents in **7** are coplanar to the macrocycle, hence contributing to increased conjugation effectively. On the other hand, smaller TPA values were measured for [28]hexaphyrin bis-gold(III) complexes. These results demonstrate clearly a common sharp drop in TPA value upon aromatic-to-antiaromatic changes. Importantly, the attenuation ratios are rather similar in a range of 0.19−0.23 (Table 1), providing a quantitative measure of how sharply aromatic-to-antiaromatic changes decrease the TPA values.[10] Despite the similar number of conjugated π-electrons and the same peripheral substituents, 5-fold decreases in the TPA value from aromatic to antiaromatic switch are remarkable, posing an important theoretical challenge.

In summary, we have developed effective synthetic routes to peripherally substituted bis-gold(III) hexaphyrins starting from the octabrominated hexaphyrin bis-gold(III) complex **4**. Expansion of π-conjugated network by the direct attachment of phenylethynyl groups led to the enhancement of TPA value. Reversible aromatic-to-antiaromatic changes of hexaphyrin bis-gold(III) complexes upon two-electron reduction and oxidation allow us to quantify the influence of the aromaticity upon TPA value for the first time.

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Supporting Information Available: Synthetic procedures and spectral data (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystallographic data for **5**: $C_{121.5}H_{56}N_6F_{30}Au_2Cl_1O_{1.5}$, $M_w = 2623.11$, monoclinic, $C2/c$ (No. 15), $a = 25.078(5)$ Å, $b = 33.677(6)$ Å, $c = 25.573(5)$ Å, $\beta = 105.052(4)°$, $V = 20856(7)$ Å^3, $D_{calcd} = 1.671$ g/cm^3, $Z = 8$, $R_1 = 0.0847$ ($I > 2.0\ \sigma(I)$), $wR_2 = 0.2434$ (all data), GOF = 1.061 ($I > 2.0\ \sigma(I)$). Crystallographic data for **7**: $C_{137}H_{48}N_6F_{30}Au_2$, $M_w = 2741.75$, triclinic, $P\bar{1}$ (No. 2), $a = 17.1064(18)$ Å, $b = 18.4071(19)$ Å, $c = 21.029(2)$ Å, $\alpha = 109.458(2)°$, $\beta = 97.070(2)°$, $\gamma = 104.393(2)°$, $V = 5891.7(11)$ Å^3, $D_{calcd} = 1.545$ g/cm^3, $Z = 2$, $R_1 = 0.0655$ ($I > 2.0\ \sigma(I)$), $wR_2 = 0.2176$ (all data), GOF = 1.079 ($I > 2.0\ \sigma(I)$).

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