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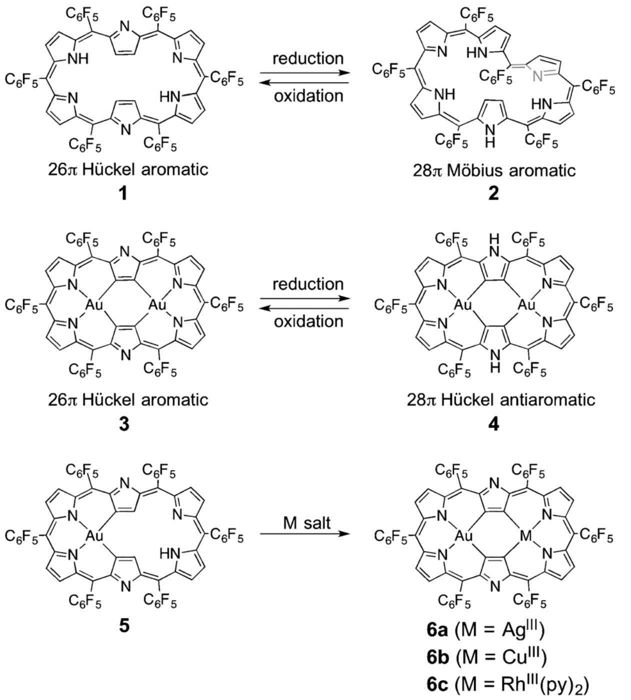
Gold^{III}–Iridium^{III} Hybrid Complexes of Hexaphyrin(1.1.1.1.1.1)

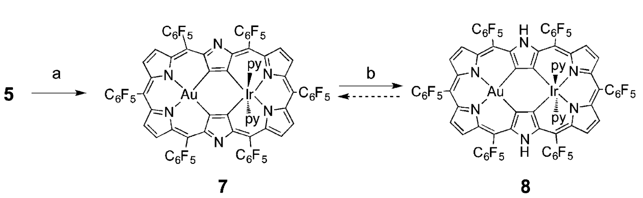
Koji Naoda, Hirotaka Mori, and Atsuhiro Osuka*[a]

In the last two decades, expanded porphyrins that possess larger pyrrolic macrocyclic rings in comparison to porphyrins have received increasing attention due to their ability to accomplish metalation with various metal ions and realize versatile electronic states.[1] One such compound reported here is [26]hexaphyrin **1**[2] that gives a range of metal complexes such as aromatic, antiaromatic,[3] Möbius aromatic,[4] Möbius antiaromatic,[5] and stable radical species,[6] depending upon the coordinated metal, the number of π-electrons participating in conjugation, and the molecular topology. [26]Hexaphyrin **1** has a planar rectangular shape harnessing 26π electrons and therefore exhibits a strong diatropic ring current, while its reduced congener, [28]hexaphyrin **2**, exists as a dynamic mixture of conformers in solution with twisted Möbius aromatic species being the predominant conformers (Scheme 1).[7] As seen for bis-Au^{III} and mono-Au^{III} complexes **3** and **5**, Au^{III}-metalation helps to rigidify the planar conformations, thus facilitating the formation of Hückel antiaromatic species occupying 28π electronic states such as **4**.[3] Mono-Au^{III} hexaphyrin complex **5**, which can be prepared by selective mono-metalation with Na[AuCl$_4$] and Ag$_3$PO$_4$,[8] has a pre-organized CCNN cavity and is a useful precursor for the preparation of hybrid bis-metal complexes such as **6a** (Au^{III}–Ag^{III}), **6b** (Au^{III}–Cu^{III}), and **6c** (Au^{III}–Rh^{III}; see Scheme 1). Stimulated by the intriguing properties and reactivities of Ir^{III}-porphyrnoids,[9,10] we examined the iridium metalation of **5**.



Scheme 1. Redox interconversions of free-base and bis-Au^{III} complexes of hexaphyrins and formation of hybrid bis-metal complexes. py = pyridine.

Initially, mono-Au^{III} hexaphyrin **5** was reacted with [IrCl(cod)]$_2$ (10 equiv) in the presence of NaOAc (10 equiv) in refluxing pyridine, by following a previously reported procedure used to prepare **6c**.[3d] Ir-metalated products were obtained in low yields with poor reproducibility. In the next step, we employed the metalation procedure used for the Ir^{III} complex of 5,10,15-tris(pentafluorophenyl)corrole.[11b] A solution of **5** in THF was refluxed in the presence of [IrCl(cod)]$_2$ and NaOAc for 3 hours under nitrogen atmosphere, to which pyridine was added, and the resulting solution was stirred for an additional 1 hour. After being passed through a short basic alumina column, [26]hexaphyrin Au^{III}–Ir^{III} complex **7** was obtained in 62 % yield after purification by silica gel column chromatography (Scheme 2). The high-resolution electrospray-ionization time-of-flight (HR-ESI-TOF) mass spectrum of **7** indicated the parent ion peak at $m/z = 2003.0560$ ($[M+H]^+$) (calcd for $C_{76}H_{19}N_8F_{30}AuIr$: $m/z = 2003.0550$). The ^{1}H NMR spectrum of **7** displays four doublet resonances corresponding to the outer-β protons in the range of 9.18–9.66 ppm and three upfield-shifted signals



Scheme 2. Ir metalation to a mono-Au^{III} hexaphyrin **5**. py = pyridine. Conditions: a) [IrCl(cod)]$_2$ (10 equiv) and NaOAc (10 equiv), then pyridine (excess) in THF. b) NaBH$_4$ (20 equiv) in CH$_2$Cl$_2$/MeOH (10:1).

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due to the axial pyridyl protons at 0.82, 4.19, and 5.38 ppm. Such resonances indicate a strong diatropic ring current present in compound **7**. Its crystal structure was determined by X-ray diffraction analysis (Figure 1 a).[12] The Ir^{III} ion is bound within the NNCC pocket in an octahedral manner with two axially coordinated pyridines completing the coordination sphere. To the best of our knowledge, Ir^{III} azuliporphyrin is the only reported example of Ir^{III} carbaporphyrinoids bearing a Ir–C bond.[10d] N(1)–Au and N(2)–Au bonds are 2.099 and 2.105 Å, respectively, which are significantly longer than the corresponding trans C–Au bonds; 1.997 Å for C(12)–Au and 2.021 for C(28)–Au. A similar feature is observed for the Ir^{III} site; 2.096 and 2.217 Å for N(4)–Ir and N(5)–Ir, and 2.010 and 2.014 Å for C(27)–Ir and C(13)–Ir (Figure 1 a). The absorption spectrum of **7** features an intense Soret-like band at 556 nm and broad Q-like bands at 706, 1150, and 1352 nm, which are characteristic of aromatic porphyrinoids (Figure 2). Nucleus-independent chemical shift (NICS) values[13] of **7** have been calculated to be large negative (see the Supporting Information), also confirming its aromatic nature.

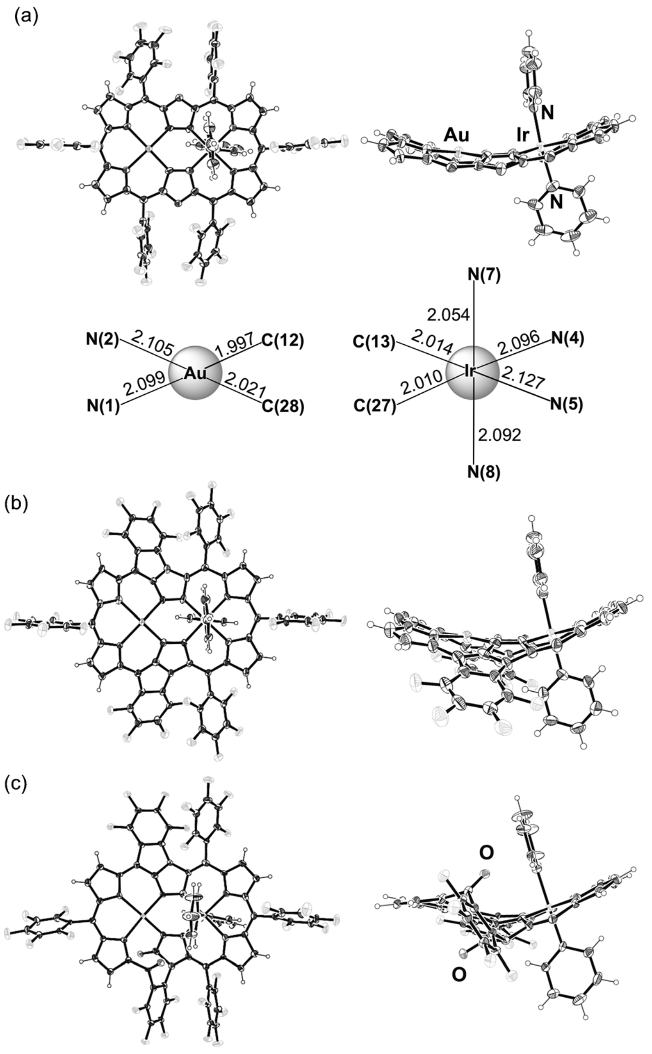


Figure 1. X-ray crystal structures of (a) **7**, (b) **9**, and (c) **12** and (a) selected bond lengths of **7**. Left: top view; Right: side view. The thermal ellipsoids are scaled to (a) 50 % probability and (b,c) 30 % probability. Solvent molecules and pentafluorophenyl groups in the side view are omitted for clarity.

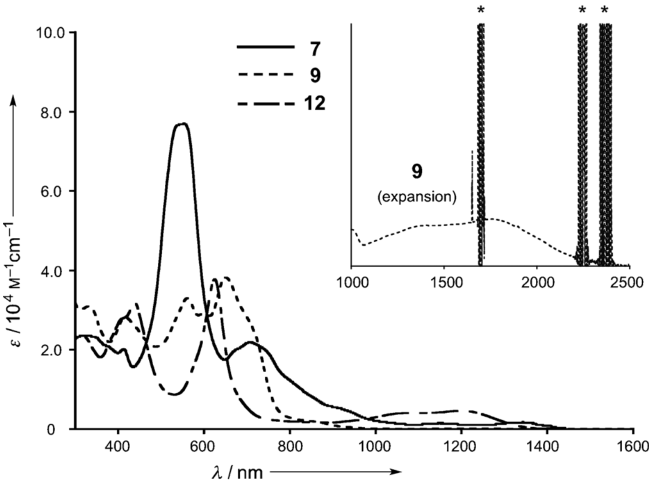
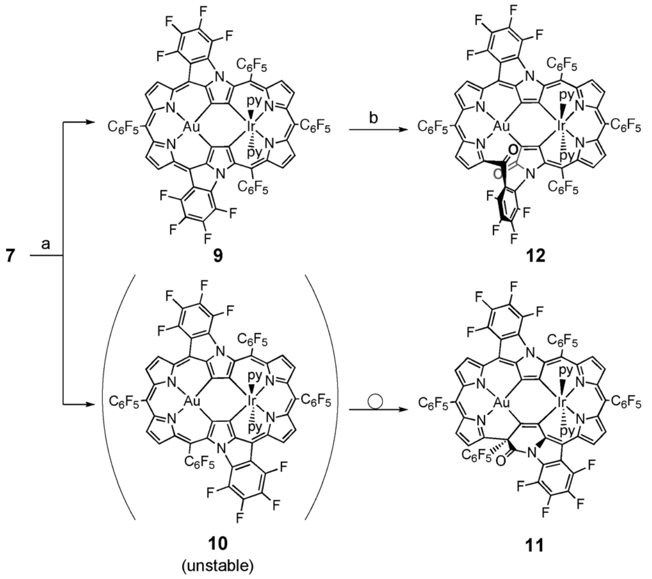


Figure 2. UV/Vis/NIR absorption spectra of **7**, **9**, and **12** in CH_2Cl_2. Peaks marked with an asterisk are originate from the solvent.

Reduction of **7** with $NaBH_4$ proceeded quantitatively to give [28]hexaphyrin Au^{III}–Ir^{III} complex **8**. The HR-ESI-TOF mass spectrum of **8** indicated the parent ion peak at $m/z =$ 2004.0641 ($[M]^+$) (calcd for $C_{76}H_{20}N_8F_{30}AuIr$: $m/z =$ 2004.0628). In the ^{1}H NMR spectrum, the outer pyrrolic NH protons are shifted to high field at −7.98 ppm, the outer-β proton resonances are in the range of −1.83–−3.02 ppm, and the axial pyridyl protons are inversely shifted downfield; α-protons at 29.39, β-protons at 14.66, and a γ-proton at 13.47 ppm, thus providing evidence of a remarkably strong paratropic ring current. The absorption spectrum of **8** shows an ill-defined Soret band and no Q-bands. Beside these features, weak absorption bands are observed at 1163, 1500, and 2000 nm, probably related to a transition to a dark state (see the Supporting Information).[14] [28]Hexaphyrin **8** is stable enough for analysis by NMR and UV/Vis/NIR spectroscopies as well as cyclic voltammetry measurements, but is gradually oxidized to **7** in solution in open air.

One tactic to lock a [28]hexaphyrin framework is to impose an intramolecular *N*-fusion reaction.[15] Thus, we examined the feasibility of *N*-fusion reactions by heating a solution of **7** in 1,2-dichlorobenzene at 150 °C. These conditions actually afforded the doubly *N*-fused hexaphyrin syn-isomer **9** in 58 % yield as a dark violet solid. A rearranged doubly *N*-fused hexaphyrin anti-isomer **11** was also obtained as a minor product. The ^{1}H NMR spectrum of hexaphyrin **9** is similar to that of **8**, indicating a strong paratropic ring current by displaying remarkably upfield-shifted outer-β proton resonances in the range of 1.55–2.43 ppm and α-, β-, and γ-protons of the axial pyridine at 19.68 ppm, 11.45 ppm, and 11.10 ppm, respectively. The lack of the two fluorine atoms at the *ortho* position of the pentafluorophenyl groups was also confirmed by ^{19}F NMR analysis. The UV/Vis/NIR spectrum shows ill-defined Soret-like bands and a low energy band in the range of 1000–2500 nm related to the transition to a dark state, which is characteristic of antiaromatic porphyrinoids (Figure 2).[14] The structure of **9** was revealed by X-ray diffraction analysis to be a syn-doubly *N*-fused product at the Au-site (Figure 1 b). The observed preferential *N*-fusion reaction at the Au-site may be rationalized in terms of electrophilicity, with the Au^{III}-complex having a more electrophilic nature when compared to the Ir^{III}-complex. Quite large positive NICS values of **9** were calculated inside the macrocycle (ca. +39 to +45 ppm).[16] This computational study also supported a strong antiaromatic nature for **9**. Fortunately, the structure of the minor product **11** has been revealed by X-ray diffraction analysis (see the Supporting Information and Scheme 3). Interestingly, one of the fused pyrroles underwent a rearrangement to form a six-membered lactam ring. Adventitious water is the most likely source of oxygen. It is conceivable that **11** is formed via an oxidative rearrangement of the putative anti-*N*-fusion product **10**.



Scheme 3. *N*-Fusion reaction of **7** and oxidative cleavage and rearrangement reaction. Conditions: a) 1,2-dichlorobenzene, 150 °C. b) MnO_2, air, CH_2Cl_2, room temperature.

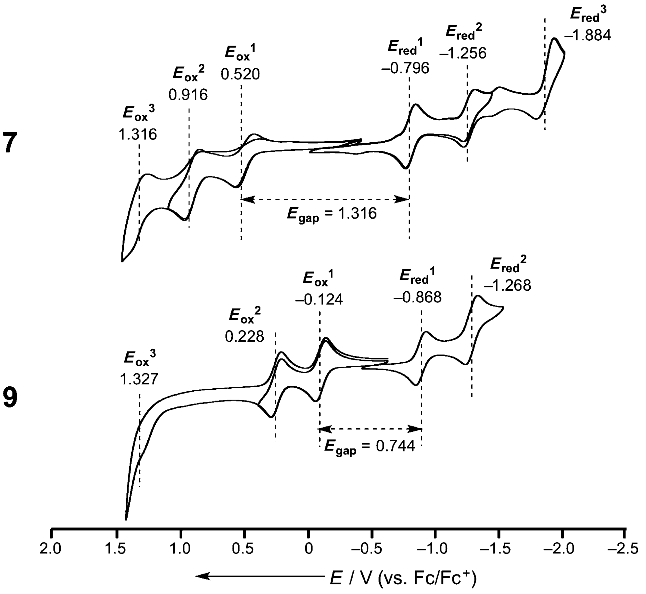


Figure 3. Cyclic voltammograms of the hexaphyrin **7** and **9** in anhydrous CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte, and Ag/AgClO$_4$ as a reference electrode. Fc/Fc$^+$ was used as an external reference.

Finally, the syn-doubly *N*-fused hexaphyrin **9** was oxidized with MnO_2, thereby giving rise to a pronounced color change from dark violet to clear green. After the standard work-up procedures, product **12** was isolated in about 50 % yield. X-ray diffraction analysis revealed the structure of **12**, in which the *meso*-carbon and pyrrolic α-carbon in one of the *N*-fused moieties is oxidatively cleaved (Figure 1 c). The covalently linked macrocyclic structure of **12** is still retained through the 1,2-tetrafluorophenylene linkage, but the macrocyclic conjugation is interrupted due to the practically orthogonal geometry of the linkage. The two carbonyl groups are arranged in a roughly antiparallel fashion with a distance of about 3 Å. The ^{1}H NMR spectrum of **12** displays eight resonances related to the pyrrolic outer-β proton in the range of 5.32–7.35 ppm, while UV/Vis/NIR spectra exhibit ill-defined Soret-like bands at 438 nm and 625 nm and a broad absorbance in the NIR region in the range of 900–1400 nm (Figure 2). Collectively, complex **12** can be assigned as a nonaromatic species; however, it is interesting to point out that there is a considerable through-space interaction between the two carbonyl groups in its LUMO and LUMO + 2 (see the Supporting Information).

The electrochemical properties of **7**, **8**, **9**, and **12** were studied by cyclic voltammetry (Figure 3 and the Supporting Information). The hexaphyrin **7** exhibits three reversible oxidations at $E_{ox} = 0.520$, 0.916, and 1.316 eV, and three reversible reductions at $E_{red} = -0.796$, -1.256, and -1.884 eV, thus indicating its electron-rich nature as compared with **3** ($E_{ox}^1 = 0.899$ and $E_{red}^1 = -0.309$) and **5** ($E_{ox}^1 = 0.945$ and $E_{red}^1 = -0.409$). The more electron-deficient nature of the Au^{III} metalation site may explain why the regioselective *N*-fusion reaction occurs there. Complexes **8** and **9** show oxidation waves at very low potentials, −0.036 and −0.436 eV for **8** and 0.228 and −0.124 eV for **9**. The very low oxidation potential values of **8** may help to explain its chemical instability. Consistent with the assignment as antiaromatic species, the electrochemical HOMO–LUMO gaps of **8** and **9** are both quite small, 0.608 and 0.744 eV, respectively.

In summary, the Au^{III}–Ir^{III} hybrid complex of [26]hexaphyrin **7** was prepared by the reaction of mono-Au^{III} [26]hexaphyrin complex **5** with $[IrCl(cod)]_2$. Complex **7** was quantitatively reduced to the corresponding [28]hexaphyrin

8, which displays an exceptionally strong paratropic ring current. Heating of **7** at 150 °C in 1,2-dichlorobenzene was found to give rise to the doubly *N*-fused [28]hexaphyrin complex syn-isomer **9**, preferentially as a locked antiaromatic species. The antiaromatic properties of **9** are highlighted by its strong paratropic ring current, small electrochemical HOMO–LUMO gap, and a characteristic low energy absorption to a dark state. The oxidation of **9** with MnO_2 caused a regioselective oxidative cleavage to form **12**. The electrochemical studies of these Au^{III}–Ir^{III} hybrid complexes helped to reveal their rather electron-rich properties as compared with Au^{III}–Au^{III} complexes. Attempts to utilize these hybrid complexes in catalytic applications are now in progress and will be reported elsewhere.

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Keywords: aromaticity · conjugation · iridium · metalation · *N*-fusion reactions

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[12] **7**: $C_{86.50}H_{30}F_{30}N_8AuIr$, $M_r = 2140.35$, monoclinic, space group $C\,2/c$ (no. 15), $a = 37.4313(7)$, $b = 20.4320(4)$, $c = 23.0628(4)$ Å, $\beta = 123.3379(7)°$, $V = 14735.8(5)$ Å^3, $Z = 8$, $T = 93(2)$ K, $D_{calcd} = 1.930$ g cm^{-3}, $R_1 = 0.0494$ ($I > 2\sigma(I)$), $R_w = 0.1327$ (all data), GOF = 1.024. **9**: $C_{103.50}H_{50}F_{28}N_8AuIr$, $M_r = 2326.68$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.4207(3)$, $b = 18.0624(3)$, $c = 18.1236(3)$ Å, $\alpha = 79.4762(8)$, $\beta = 66.0833(8)$, $\gamma = 70.4275(8)°$, $V = 4341.97(13)$ Å^3, $Z = 2$, $T = 93(2)$ K, $D_{calcd} = 1.780$ gcm^{-3}, $R_1 = 0.0807$ ($I > 2\sigma(I)$), $R_w = 0.2233$ (all data), GOF = 1.019. **11**: $C_{79}H_{21}F_{28}N_8Cl_9OAuIr$, $M_r = 2338.28$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.5292(3)$, $b = 17.0762(3)$, $c = 31.3703(7)$ Å, $\alpha = 88.9864(7)$, $\beta = 76.4613(7)$, $\gamma = 73.5625(10)°$, $V = 7746.5(3)$ Å^3, $Z = 4$, $T = 93(2)$ K, $D_{calcd} = 2.012$ gcm^{-3}, $R_1 = 0.1049$ ($I > 2\sigma(I)$), $R_w = 0.2788$ (all data), GOF = 1.032. **12**: $C_{81}H_{18}F_{28}N_8Cl_{15}O_2AuIr$, $M_r = 2587.95$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.4959(3)$, $b = 17.0293(3)$, $c = 20.4860(6)$ Å, $\alpha = 107.2492(8)$, $\beta = 99.2652(8)$, $\gamma = 113.1859(13)°$, $V = 4211.49(17)$ Å^3, $Z = 2$, $T = 93(2)$ K, $D_{calcd} = 2.041$ g cm^{-3}, $R_1 = 0.0666$ ($I > 2\sigma(I)$), $R_w = 0.1737$ (all data), GOF = 1.007. CCDC 927539 (**7**), CCDC 927538 (**9**), CCDC 927537 (**11**), and CCDC 927536 (**12**) contain 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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[16] NICS values of **8** have been also calculated on the basis of the optimized structure, which indicates larger positive values than **9**. Taking this and the very strong paratropic ring current into consideration, the antiaromaticity of **8** is regarded exceptionally strong (see also the Supporting Information).

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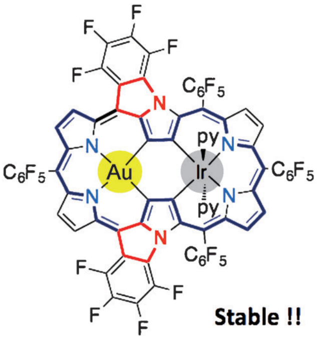
Au revoIR: Hexaphyrin Au^{III}–Ir^{III} complexes were prepared from the reaction of a mono-Au^{III} [26]hexaphyrin complex with $[IrCl(cod)]_2$ followed by treatment with pyridine. *N*-Fusion reaction of this complex gave a syn-doubly *N*-fused hexaphyrin as the major product, which displayed antiaromatic properties such as strong paratropic ring current, a small HOMO–LUMO gap and a low-energy forbidden absorption. The oxidation of this fused product with MnO_2 afforded an oxidatively cleaved product.



Stable !!

28π Hückel Antiaromatic

Hybrid Complexes

*Koji Naoda, Hirotaka Mori, Atsuhiro Osuka** ▮▮▮▮–▮▮▮▮

$Gold^{III}$–$Iridium^{III}$ Hybrid Complexes of Hexaphyrin(1.1.1.1.1.1)