Luminescent Au(III) organometallic complex of N-confused tetraphenylporphyrin†

Motoki Toganoh, Teppei Niino and Hiroyuki Furuta*

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An organometallic Au(III) complex of N-confused tetraphenylporphyrin has been synthesized and its electrochemical and photophysical properties investigated; unique emission is observed in solution at ambient temperature.

The luminescence of organometallic transition metal complexes has been receiving considerable attention because of its promising applications in organic light-emitting devices, photocatalysis and bio-imaging.[1] These complexes are often accompanied by C_{sp^2}–metal or C_{sp}–metal bonds, which are important for improved emission efficiency. For example, Ir(III)(N^C-ppy)$_3$ (**1**) is an efficient triplet green emitter[2] and Au(III)(C^N^C-dpp)(C≡CPh) (**2**)[3] is a rare example of a luminescent Au(III) complex at room temperature (Chart 1). In this context, studies on the photochemistry of carbaporphyrin metal complexes would be fascinating because they usually have C_{sp^2}–metal bonds and also have rigid structures, which is also favorable for efficient emission.[4] However, these studies have yet to be undertaken fully due to lack of available emissive compounds. Here, we report a new luminescent Au(III) complex, N-confused tetraphenylporphyrin (NCTPP)[5] Au(III) (**3**). This is not only the first example of an emissive organometallic carbaporphyrinoid but is also a rare example of an emissive Au(III) complex, even at room temperature.[6] Note that standard porphyrin Au(III) complexes are emissive only at lower temperatures.[7]

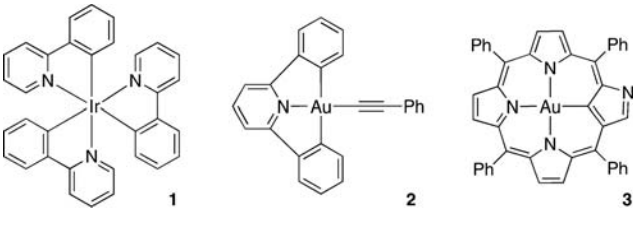
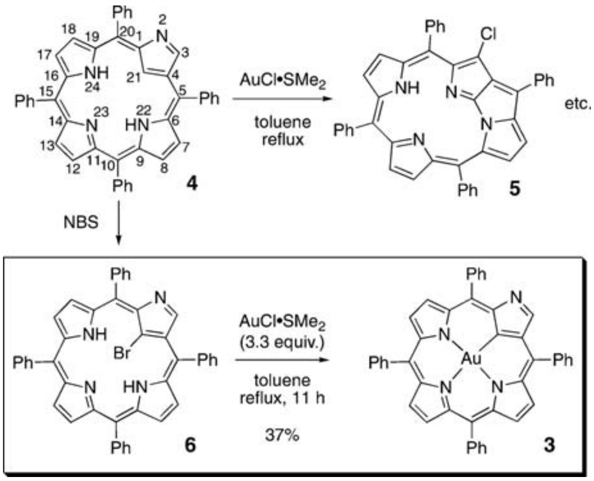


Chart 1 Luminescent organometallic transition metal complexes.

Au(III) complex **3** was obtained through a reaction with AuCl·SMe$_2$ (Scheme 1). The reaction of AuCl·SMe$_2$ with NCTPP (**4**) was not efficient, affording only a trace amount of **3** due to competitive side reactions. While complete separation was difficult, chlorinated N-fused tetraphenylporphyrin (**5**) and 21-Cl-NCTPP were detected in the crude product.[8,9] These unexpected side reactions could be avoided by prior bromination of **4** with *N*-bromosuccinimide (NBS).[8] **3** was obtained in 37% yield upon treating 21-Br-NCTPP (**6**) with 3.3 equivalents of AuCl·SMe$_2$ in toluene under reflux for 11 h. The product was stable under usual experimental conditions and could be isolated by standard silica gel column chromatography. The ^{1}H NMR, ^{13}C NMR and mass spectra of **3** are consistent with its structure. For example, the signal attributable to the proton at the C3 position is observed at δ 9.43, but no signal due to NH protons is detected. The ^{13}C NMR spectrum resembles that of the NCTPP Ag(III) complex,[10] and the parent ion peak is observed at m/z = 809.19395 (calc. for MH$^+$: 809.19795) in the mass spectrum (ESI positive mode).



Scheme 1 The preparation of **3**.

The structure of **3** was confirmed by X-ray crystallographic analysis (Fig. 1).‡ The Au atom is placed in the center of the macrocycle. The C_{sp^2}–Au bond length is 2.016(12) Å, which is shorter than those of **2** (2.073(7) and 2.071(7) Å) and longer than the C_{sp}–Au bond length of **2** (1.979(7) Å).[3a] The N–Au bond lengths (average 2.044 Å) are longer than that of tetraphenylporphyrin Au(III) complex ([Au(TPP)]$^+$[AuCl$_4$]$^-$, average 2.017 Å).[11] The N-confused porphyrin plane deviates from planarity, where the root mean-square deviation for the 24 heavy atoms is 0.252 Å (Fig. 1(b)). Because no axial ligand or counterion is found, unlike standard porphyrin Au(III) complexes,[7,12] **3** forms an intermolecular stacking array in the solid state (Fig. 2). The inter-plane distances (3.954 and 4.006 Å) are significantly longer than those of common π–π

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. E-mail: hfuruta@cstf.kyushu-u.ac.jp
Fax: +81 92-802-2865; Tel: +81 92-802-2865

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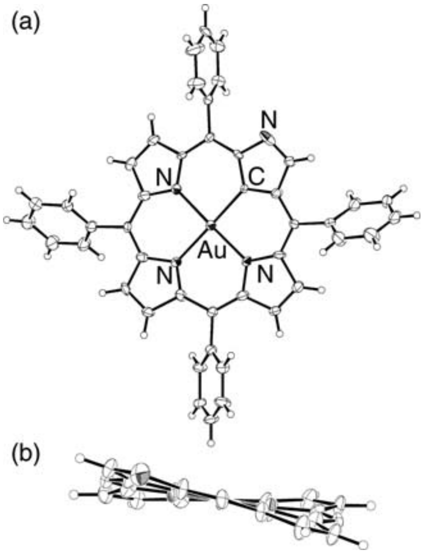

Fig. 1 Crystal structure of **3**: (a) top view, (b) side view. Solvent molecules are omitted and the phenyl groups are removed in (b) for clarity. Thermal ellipsoids are shown at the 30% probability level.

stacked porphyrin arrays (3.4–3.6 Å)[13] because of steric repulsion imposed by the *meso*-phenyl groups. The intermolecular Au–Au distances are long (5.132 and 5.060 Å) and no metal–metal interactions are found in the solid state.

The absorption spectra of **3** and **4** in CH_2Cl_2 are shown in Fig. 3. In the absorption spectrum of **3**, the Soret band is observed at 436 nm, and the Q-bands are observed at 513, 549 and 636 nm. The remarkable blue shift of the Q-bands from **3** to **4** is caused by lowering of the HOMO energy level (*vide infra*). In the electrochemical measurements of **3**, the first oxidation potential (E_{ox}) is found at +0.53 V (reversible, *vs.* Fc/Fc^+) and the first reduction potential (E_{red}) is found at –1.54 V (irreversible). The relatively large $|E_{ox} - E_{red}|$ value of **3** (2.07 V) is consistent with the blue shift seen in the absorption spectrum.[14]

The low-lying HOMO energy level of **3** is supported by a theoretical study. The calculated Kohn-Sham orbitals of **3** and **4** are shown in Fig. 4. The calculation was achieved by the B3LYP method, with the SDD basis set for Au and the 6-31G** basis set for the other atoms (denoted as B3LYP/631S). Basically, the HOMO and LUMO of **3** are mainly composed of porphyrin π-orbitals and resemble those of **4**, except for a small contribution of the d-orbitals of the Au atom. Although the LUMO energy level of **3** is similar to that of **4**, the HOMO energy level of **3** is significantly lower than that of **4**. In the HOMO of **3**, a large coefficient on the carbon atom and small coefficients on the three nitrogen atoms are observed in the NNNC core. As a result, moderate interaction between the metal d-orbital and the porphyrin π-orbital is expected, which may result in stabilization of the HOMO energy level. In contrast, only small coefficients on the two internal nitrogen atoms are found in the LUMO of **3**, and thus the interaction would be trivial.

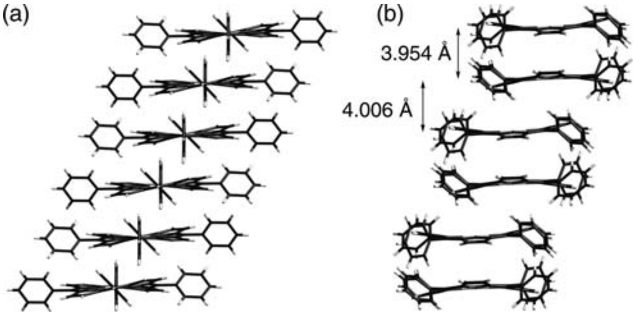

Fig. 2 Intermolecular stacking diagram of **3** in the solid state. The viewpoints are different in (a) and (b).

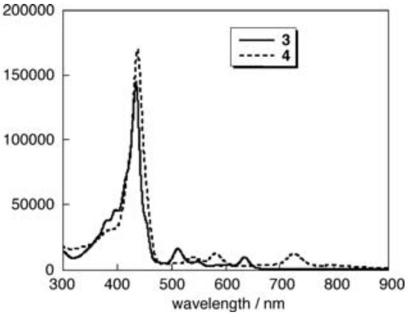

Fig. 3 Absorption spectra of **3** and **4** in CH_2Cl_2.

Interestingly, **3** shows a distinct emission at ambient temperature, rare example among Au(III) complexes.[15] The unique emission profile of **3** in CH_2Cl_2 is shown in Fig. 5, and the photophysical properties of **3** in various solvents are listed in Table 1. Emission peaks are observed at 650, 707 and 789 nm in CH_2Cl_2, where the intensity of the last one is the largest. The emission quantum yield is 2.3×10^{-4}, which is comparable to those of **2** and its derivatives.[3] Despite the unique emission profile, almost no solvent effect was found among the various solvents we investigated (toluene, THF and MeOH). While the emission mechanism is totally unknown at present, multiple pathways, like the cases of standard porphyrin Au(III) complexes,[7] are inferred from our preliminary photophysical measurements. The emission peaks corresponding to λ_{em1} and λ_{em2} could be explained by fluorescence from the S_1 state, because they resemble those of free-base NCTPP (**4**).[16,17] The large Stokes shift for λ_{em3} (3049 cm^{-1}) and the existence of a heavy atom in **3** imply phosphorescence from the T_1 state, but

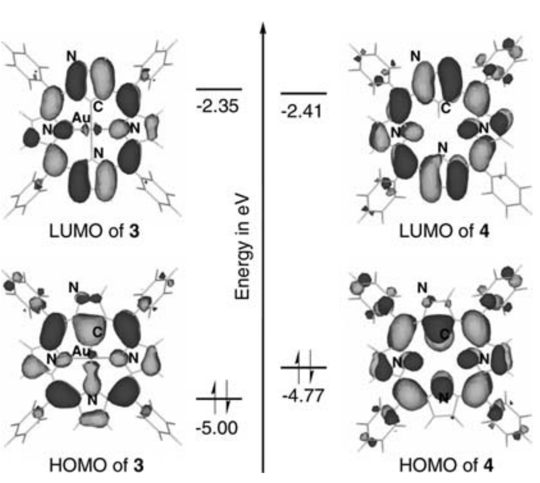

Fig. 4 Kohn-Sham orbitals and their energy levels for **3** and **4**, calculated at B3LYP/631S level.

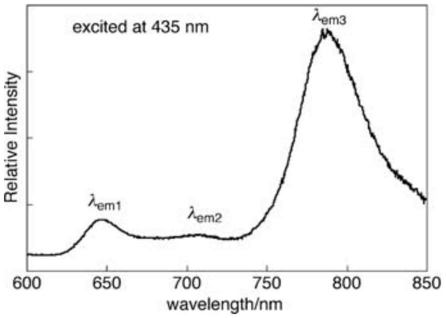

Fig. 5 Emission spectrum of **3** in CH_2Cl_2 at ambient temperature.

Table 1 Photophysical properties of **3**

Solvent	Soret^a	$Q_1{}^a$	$Q_2{}^a$	$Q_3{}^a$	$\lambda_{em1}{}^a$	$\lambda_{em2}{}^a$	$\lambda_{em3}{}^a$	$\Phi_{em}{}^b$
Toluene	438	515	551	639	654	701	790	2.3
CH_2Cl_2	435	515	549	636	650	707	789	2.9
THF	435	513	549	636	646	705	784	2.2
MeOH	432	510	sh^c	636	651	693	794	2.6

^{a} Wavelength in nm. ^{b} Emission quantum yields ($\times 10^{-4}$) based on relative intensity to tetraphenylporphyrin.[16] ^{c} sh = shoulder.

the lifetimes obtained so far are quite short,[18] and a detailed study is essential for further discussion.

Emission from **3** might be facilitated by electron donation from the ligand to the metal center. In contrast to the rich luminescent properties of Au(I) complexes, Au(III) complexes have rarely been observed to emit.[15] Au(III) has a d^8 electronic configuration and usually forms square-planar complexes. Such planar Au(III) complexes have low-energy ligand field d–d transitions due to the electron-poor nature of the Au(III) center, and these transitions are assumed to be a key factor in quenching the luminescence of Au(III) complexes. To impair this factor, one suggested strategy is the introduction of an electron-donating ligand, such as an alkynyl group, to the Au(III) center, such as in **2**.[3] In the case of **3**, electron donation from the confused pyrrole to the Au(III) atom through the C_{sp^2}–Au(III) bond might contribute to the relatively electron rich Au(III) center, which results in a raising of the energy of the d–d transitions high enough to inhibit emission quenching.

In summary, we have synthesized an NCTPP Au(III) complex, **3**, and revealed its structure by X-ray crystallographic analysis. It displays a distinct emission in solution at ambient temperature, where no solvent effect is observed. This rare example of a luminescent Au(III) complex might be attributed to facile electron donation from the confused pyrrole to the Au(III) atom through the C_{sp^2}–Au(III) bond, implying new potential for the *confusion* approach. Aided by the rich chemistry of porphyrin Au complexes,[19] the further development of N-confused porphyrin Au complexes can be expected, and a detailed study of their unique photophysical properties is now under way.

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Notes and references

‡ Crystal data for **3**, violet prism, $C_{44}H_{27}AuN_4{\cdot}CH_2Cl_2$, $M_w = 893.59$, monoclinic, space group $P2_1/c$ (no. 14), $a = 8.9794(12)$, $b = 15.034(2)$, $c = 25.640(3)$ Å, $\beta = 91.826(3)°$, $V = 3459.5(8)$ Å^3, $Z = 4$, $T = 243$ K, 18 755 reflections measured, 6252 unique data ($R_{int} = 0.1045$), $R = 0.0782$ ($I > 2\sigma(I)$), $R_w = 0.1872$ (all data), GOF on $F^2 = 1.019$ (all data).†

1 (*a*) W.-Y. Wong, *Dalton Trans.*, 2007, 4495; (*b*) A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 2004, **248**, 273.
2 K. A. King, P. J. Spellane and R. J. Watts, *J. Am. Chem. Soc.*, 1985, **107**, 1431.
3 (*a*) V. W.-W. Yam, K. M.-C. Wong, L.-L. Hung and N. Zhu, *Angew. Chem., Int. Ed.*, 2005, **44**, 3107; (*b*) C. W. Chan, W. T. Wong and C. M. Che, *Inorg. Chem.*, 1994, **33**, 1266.
4 (*a*) T. D. Lash, *Synlett*, 1999, 279; (*b*) M. Stępień and L. Latos-Grażyński, *Acc. Chem. Res.*, 2005, **38**, 88.
5 (*a*) H. Furuta, T. Asano and T. Ogawa, *J. Am. Chem. Soc.*, 1994, **116**, 767; (*b*) P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz and T. Głowiak, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 779.
6 T. D. Lash, D. A. Colby and L. F. Szczepura, *Inorg. Chem.*, 2004, **43**, 5258.
7 (*a*) A. Antipas, D. Dolphin, M. Gouterman and E. C. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 7705; (*b*) M. P. Eng, T. Ljungdahl, J. Andréasson, J. Mårtensson and B. Albinsson, *J. Phys. Chem. A*, 2005, **109**, 1776; (*c*) J. Andréasson, G. Kodis, S. Lin, A. L. Moore, T. A. Moore, D. Gust, J. Mårtensson and B. Albinsson, *Photochem. Photobiol.*, 2002, **76**, 4700.
8 (*a*) H. Furuta, T. Ishizuka, A. Osuka and T. Ogawa, *J. Am. Chem. Soc.*, 1999, **121**, 2945; (*b*) H. Furuta, T. Ishizuka, A. Osuka and T. Ogawa, *J. Am. Chem. Soc.*, 2000, **122**, 5748.
9 (*a*) A. Młodzianowska, L. Latos-Grażyński, L. Szterenberg and M. Stępień, *Inorg. Chem.*, 2007, **46**, 6950; (*b*) M. Toganoh, T. Ishizuka and H. Furuta, *Chem. Commun.*, 2004, 2464; (*c*) M. Toganoh, S. Ikeda and H. Furuta, *Chem. Commun.*, 2005, 4589; (*d*) M. Toganoh, S. Ikeda and H. Furuta, *Inorg. Chem.*, 2007, **46**, 10003.
10 H. Furuta, T. Ogawa, Y. Uwatoko and K. Araki, *Inorg. Chem.*, 1999, **38**, 267.
11 A. M. Shachter, E. B. Fleischer and R. C. Haltiwanger, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, **C43**, 1876.
12 R. Timkovich and A. Tulinksy, *Inorg. Chem.*, 1977, **16**, 962.
13 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525.
14 While exact potentials for **4** cannot be measured, probably due to NH tautomerism, $|E_{ox} - E_{red}|$ is estimated to be $1.7\sim1.8$ V from those of related compounds: (*a*) H. Furuta, T. Ishizuka, A. Osuka, H. Dejima, H. Nakagawa and Y. Ishikawa, *J. Am. Chem. Soc.*, 2001, **123**, 6207; (*b*) M. Toganoh and H. Furuta, *Chem. Lett.*, 2005, **34**, 1034.
15 A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 2001, **219–221**, 489.
16 (*a*) J. P. Belair, C. J. Ziegler, C. S. Rajesh and D. A. Modarelli, *J. Phys. Chem. A*, 2002, **106**, 6445; (*b*) J. L. Shaw, S. A. Garrison, E. A. Alemán, C. J. Ziegler and D. A. Modarelli, *J. Org. Chem.*, 2004, **69**, 7423.
17 Preliminary lifetime measurements for **3** afforded two lifetimes (1.8 ns (18%) and 7.1 ns (82%)) in toluene at 650 nm.
18 Similar lifetimes but a different ratio from that measured at 650 nm are observed for **3** at 790 nm (1.7 ns (56%) and 7.0 ns (44%)).
19 (*a*) C. Y. Zhou, P. W. H. Chan and C. M. Che, *Org. Lett.*, 2006, **8**, 325; (*b*) R. W. Y. Sun, W. Y. Yu, H. Sun and C. M. Che, *ChemBioChem*, 2004, **5**, 1293; (*c*) L. Flamigni, F. Barigelletti, N. Armaroli, J.-P. Collin, I. M. Dixon, J.-P. Sauvage and J. A. G. Williams, *Coord. Chem. Rev.*, 1999, **190–192**, 671.