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# N-Confused Porphyrin Metal Complexes with an Axial Pyridine Directly Tethered from an Inner Carbon: A Bioinspired Ligand as Versatile Platform for Catalysis

Takaaki Miyazaki, Takaaki Yamamoto, Shunichi Mashita, Yuya Deguchi, Kazuki Fukuyama, Masatoshi Ishida, Shigeki Mori, and Hiroyuki Furuta\*

**Abstract:** Bioinspired pentadentate ligand, N-confused porphyrin (NCP) bearing a 2-mercaptopyridine group (1), and its  $Ru^{II}$  and  $Co^{III}$  complexes, **Ru(CO)-1a** and **Co(NO<sub>2</sub>)-1**, were synthesized and the structures were revealed by single crystal X-ray analysis. Installation of an axial thiopyridine ligand negatively shifted the redox potentials and enhanced the catalytic activity largely, which was demonstrated in the cyclopropanation reaction using the Co complex.

#### Introduction

Mimicking the active sites of heme enzymes has been considered as one of the promising strategies for development of the metalloporphyrin-based catalysts.<sup>1</sup> The original family of enzymes is responsible for various organic transformation reactions in biological systems under mild conditions.<sup>1d,2</sup> A key component of the active sites of heme enzymes is the axial donor moiety derived from the histidine (imidazole) or cysteine (thiol) residue, which plays an important role in tuning the catalytic activity (Figure 1b). In particular, the donating property of axially coordinated ligands largely facilitates the dioxygen activation on the iron center in the tetrapyrrolic macrocycles.<sup>1-3</sup> On this basis, a variety of biomimetic/bioinspired model complexes such as imidazoletethered metalloporphyrins have been synthesized,<sup>1,3</sup> however, the limited synthetic accessibility often hampers a wide-scale use of such catalysts.

Within the scope of artificial mutants of metalloporphyrin catalysts, we have been working on N-confused porphyrin (termed as NCP) since its discovery.<sup>4</sup> NCP is an isomer of porphyrin containing an inverted pyrrole subunit, and from the viewpoint of catalytic property, corresponding metallo-NCPs have shown the advantage of stabilizing high-valent metal ions due to the strong  $\sigma$ -donation of the carbon atom present in the NNNC coordination environment.<sup>5</sup> This is realized by the unique NH

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tautomeric resonance effect; the distinct 3H-tautomer having two

NHs and one CH in the core can serve as a trianionic ligand in

metal complexation (Figure 1a). In contrast, the 2H-tautomer has

one NH and one CH in the core, and one NH at the periphery,

which ordinary provides a dianionic coordination environment.

Furthermore, the unsymmetrical structures of metallo-NCPs

enabled the highly stereo-selective cyclopropanation of alkenes by rhodium-NCP<sup>6</sup> and oxygen atom transfer by rhenium-NCP.<sup>7</sup>

*Figure 1.* (a) NH-tautomerism-coupled transformation of N-confused porphyrin metal complexes; (b) Active site of horseradish peroxidase (HRP) enzyme (PDB-1H5L); (c) Schematic illustration of the biomimetic heme-type model complex studied in this work.

In this study, we have designed novel pentadentate NCP ligands with an axial pyridine moiety utilizing the regioselective substitution reaction at the inner carbon of the NCP core. This modification induced the formation of another type of tautomeric form, 3H'-tautomer, possessing one NH and one CH<sub>2</sub> (sp<sup>3</sup> carbon atom) in the core (Figure 1a).<sup>8</sup> Notably, the NCP metal complexes M-1 (e.g., Ru(CO)-1 and Co(NO<sub>2</sub>)-1, as representatives for ruthenium(II) and cobalt(III) complexes, respectively) with an axial 2-thiopyridine unit covalently linked to the inner carbon atom were prepared in a short-step from the NCP ligand 2 (Figure 1c). Such axially modified complexes could work as a new type of bioinspired catalyst.<sup>9</sup> Herein, we examined the cyclopropanation of styrene using the cobalt catalysts to evaluate the effect of introduced axial 2-thiopyridine ligand intramolecularly, because the catalytic activity of cobalt(II) NCPs for the cyclopropanation reaction was already shown by Zeigler and co-workers.<sup>10</sup> As a result, installation of the axial ligand was revealed to accelerate the catalytic reaction significantly.

#### **Results and Discussion**

Synthesis of the complex Ru(CO)-1a is simple and straightforward. At first, treatment of freebase NCP 2a with Ru<sub>3</sub>(CO)<sub>12</sub> in chlorobenzene at 140 °C and succeeding addition of pyridine at room temperature afforded Ru(CO)-3a with an axial pyridine ligand (step a in Scheme 1). The <sup>1</sup>H NMR spectrum displayed the multiplet signals at the aromatic region from  $\delta$  7.46 to 7.88 ppm along with the characteristic peripheral NH signal of the confused pyrrole ring at 9.38 ppm in CDCl<sub>3</sub>, which indicates the formation of 2H-type tautomer (Figure S6). The characteristic upfield signals at 4.70 (ortho-), 6.09 (meta-), and 6.69 (para-) ppm could be assigned as the coordinated pyridine molecule on the ruthenium center. The explicit structural evidence of Ru(CO)-3a came from the X-ray crystallographic analysis (Figure S5b, Table S2).<sup>11</sup> Like the parent ruthenium tetraphenylporphyrin complex,<sup>12</sup> Ru(CO)-3a adopts an octahedral geometry and the ruthenium metal cation is accommodated at the equatorial NNNC coordination site with CO and pyridine at the both axial positions. The complex is neutral and the valence state of the ruthenium center is +2 (d<sup>6</sup>), which is consistent with the diamagnetic character as shown in the NMR spectrum.



(a) i) Ru<sub>3</sub>(CO)<sub>12</sub>, chlorobenzene, reflux, N<sub>2</sub>, 18 h; ii) pyridine, rt, 1 h, 71%; (b) 2-mercaptopyridine, 1,2-dichloroethane, reflux, 18 h, 69%; (c) Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2-mercaptopyridine, NaNO<sub>2</sub>, THF, reflux, 1 day, 56% for Co(NO<sub>2</sub>)-1a, 40% for Co(NO<sub>2</sub>)-1b; (d) Ni(acac)<sub>2</sub>, CHCl<sub>3</sub>, reflux, N<sub>2</sub>, 1 day, 80% for Ni-3a, 82% for Ni-3b; (e) 2,2'-dithiopyridine, MeCN, reflux, 3 h, 66% for 1a, 39% for 1b; (f) Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, THF, reflux, N<sub>2</sub>, 2 h, 63% for Co(NO<sub>2</sub>)-1a, 47% for Co(NO<sub>2</sub>)-1b.

**Scheme 1.** Synthetic routes for ruthenium and cobalt complexes of NCP with an axial 2-thiopyridine group tethered from the inner carbon.

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Next, Ru(CO)-3a was treated with an excess amount of 2mercaptopyridine, then a new complex Ru(CO)-1a, in which the adjacent sulfur atom is connected to the inner carbon atom of NCP, was formed (step b in Scheme 1). The X-ray structure shows the presence of an axial 2-thiopyridine moiety connected to the sp<sup>3</sup> inner carbon atom (Figure 2a, Table S2).<sup>11</sup> This modification lead to a stronger bonding of the pyridine ligand as inferred from the shorter bond length between the ruthenium center and pyridine nitrogen in Ru(CO)-1a than that of Ru(CO)-3a (2.172(3) Å vs 2.200(5) Å, respectively) (Figure S5). Interestingly, due to the formation of 5-member ring, the pyridine ring of Ru(CO)-1a aligns along the C-Ru-N axis, whereas that of Ru(CO)-3a is tilted by ca. 33° to the axis. The bond lengths around the inner carbon atom of Ru(CO)-1a are elongated compared to those of Ru(CO)-3a (C1-C2 = 1.472(5) vs 1.409(7), C2-C3 = 1.479(5) vs 1.399(9), C2-Ru = 2.118(3) vs 2.015(5), and C2-S = 1.843(5) Å) and appropriate feature in the bond angles for sp<sup>3</sup> carbon were observed (approximately 109° for  $\angle$ C3–C2– S). Consequently, the distinct  $18\pi$ -conjugated circuit in the annulenic core of Ru(CO)-1a can be inferred from NMR spectroscopy (Figure S7). Namely, the representative features, the lack of outer NH signal and appearance of peripheral α-CH signal of the confused pyrrole ring in the typical aromatic region (9.35 ppm), were observed in CDCl<sub>3</sub>. In addition, the axially coordinated pyridine-CH signals are significantly upfield shifted to 6.05 (para-), 5.41 (meta-), 5.27 (meta-), and 2.59 (ortho-) ppm due to the diatropic ring current effect of the macrocycle. The <sup>13</sup>C NMR spectrum also supports the proposed structure; the sp<sup>3</sup> hybridized carbon signal was observed at 44.9 ppm (Figure S8). Therefore, the complex Ru(CO)-1a is composed of a 3H'-type resonance form of NCP.



Figure 2. X-ray structures of (a) Ru(CO)-1a and (b) Co(NO<sub>2</sub>)-1b. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The aforementioned protocol was applicable to the synthesis of cobalt complex in a one-step fashion. That is, treatment of **2a** with 2-mercaptopyridine in the presence of  $Co(NO_3)_2 \cdot 6H_2O$  in refluxing THF afforded the corresponding complex ( $Co(NO_2)$ -1a) in 56% yield (step c in Scheme 1). Likewise, the derivative bearing *meso*-(4-methoxylphenyl)-substituents ( $Co(NO_2)$ -1b) could be synthesized and the structure was successfully proved by X-ray analysis (Figure 2b, Table S3).<sup>11</sup> A cobalt atom is located in the NNNC coordination sphere with a nitrite anion as an axial ligand. As with Ru(CO)-1a, the covalently tethered thiopyridine moiety is present, forming the octahedral geometry. The resulting d<sup>6</sup> cobalt(III) complex with

3H'-form structure was again inferred from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Figures S13 and S14).

In an effort to verify the versatile coordination ability of the pentadentate NCP ligand, the freebase ligand 1 bearing a 2thiopyridine unit was separately prepared by heating the nickel(II) NCP complexes (Ni-2a and Ni-2b) with 2,2'-dithiopyridine in acetonitrile (step e in Scheme 1). The structure of 1a was unambiguously characterized by X-ray crystallography (Figure 3, Table S3).<sup>11</sup> The pyridine moiety is linked at the inner carbon and the confused pyrrole moiety is inclined at 38° from a mean-plane consisting of four meso-carbon atoms due to the steric congestion. Unlike the case of Co(NO<sub>2</sub>)-1a, the 3H-type tautomeric structure with a modified sp<sup>2</sup>-inner carbon atom is retained as inferred from the  $\angle$ C–N1–C bond angle (106.9°) of the confused pyrrole ring as well as the <sup>1</sup>H NMR spectrum. Reflecting the deshielding effect of the NCP ring, the proton signals of the pyridyl moiety atop were also upfield shifted (Figure S9). As expected, the resulting thiopyridine-functionalized NCP ligand 1 afforded the corresponding cobalt(III) complexes, Co(NO2)-1a/1b in good vields (step f in Scheme 1).<sup>13</sup>



*Figure 3.* X-ray structures of **1a**; (a) side and (b) top views. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The electrochemical properties of Ru(CO)-1a and Co(NO<sub>2</sub>)-1a were investigated using cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M n-tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>). Two reversible oxidation peaks at 0.34 and 0.79 V and irreversible reduction peak at -1.39 V (vs an ferrocene/ferrocenium couple, Fc/Fc<sup>+</sup>) were observed for Ru(CO)-1a (Figure S4, Table S1). In comparison with Ru(CO)-3a, the overall potentials are positively shifted due to the intrinsic electronic effect of the NCP ligand tautomers (3H'-form vs 2Hform). The resulting HOMO-LUMO gap of 1.73 eV for Ru(CO)-1a is larger than that of Ru(CO)-3a (1.58 eV), which is consistent with the blue-shifted longest-wavelength transition in the absorption spectra (Figure S1). In the case of Co(NO<sub>2</sub>)-1a, on the other hand, three irreversible oxidation peaks at 0.67, 0.79, and 1.07 V and four irreversible reduction peaks at -1.10, -1.26, -1.50, and -1.70 V were observed (Figure S4, Table S1). Although details of the irreversibility of Co(NO<sub>2</sub>)-1a on CV is unclear at this moment, it is probably related to the affinity strength between the cobalt center and the axial ligands. The first reduction potential is considerably negatively-shifted compared to that of cobalt(III) tetrakis(4carboxyphenyl)porphyrin chloride, -0.56 V (in 0.1 M TBAPF<sub>6</sub>/DMSO),<sup>14</sup> which suggests the strongly electron-donating nature of the 2-thiopyridine molety in Co(NO2)-1a. The oxidation potentials of  $Co(NO_2)$ -1a are affected similarly. Accordingly, the axial thiopyridine donor induced lowering of the oxidation potentials, which infers its potency as oxidation and/or carbene insertion catalysts.<sup>15,16</sup>

 $\ensuremath{\textbf{Table 1}}$  . Yields and stereo-selectivity for cyclopropanation of styrene with EDA



<sup>[a]</sup> The yields and *trans/cis* ratios were determined by GLC using tridecane as an internal standard. <sup>[b]</sup> The dimer is diethyl maleate ester (*Z* form). <sup>[c]</sup> At 80 °C, 6 h. <sup>[d]</sup> Isolated yield. <sup>[e]</sup> The trans/cis ratios were determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>[f]</sup> 0.1 mol% of cobalt catalyst. cp: cyclopropanated product.



*Figure 4.* The time course of cyclopropanation reactions (2, 5, 10, 20, 30, 45, and 60 min) with **Co-1a**<sub>red</sub> (blue), **Co-4** (red), and **Co<sup>II</sup>-TPP** (green).

To illustrate the catalytic capability of metalated **1**, cyclopropanation of styrene was investigated using cobalt complexes as a test reaction (Table 1). At first, **Co(NO<sub>2</sub>)-1a** was subjected to the reaction (conditions: catalyst (0.5 mol%), styrene (5 equiv), ethyl diazoacetate (EDA, 1 equiv), aerobic, in toluene). At room temperature, the reaction did not proceed. When the reaction temperature was raised at 80 °C for 6 h, cyclopropane product was obtained in 70% yield (*trans/cis* = 83/17, entry 1). Next, **Co(NO<sub>2</sub>)-1** was pretreated with 0.5% Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> aq in

dichloromethane to form the reduced species, Co-1a<sub>red</sub> and Co-1bred, and subjected to the catalytic reactions at room temperature for 1 h. For comparison, cobalt(II) complex of the N-methylated Nconfused tetraphenylporphyrin with pyridine as an axial ligand, (Co-4),<sup>1</sup> cobalt(II) Co<sup>"</sup>(*N*-MeNCTPP)(py) and tetraphenylporphyrin (Co<sup>II</sup>-TPP) were used as reference catalysts. The time course of cyclopropanation reactions with Co-1<sub>red</sub>, Co-4, and Co<sup>II</sup>-TPP catalysts were also followed (Figure 4). As a result, Co-1<sub>red</sub> exhibited 78% yield with 92/8 trans/cis-selectivity (entry 2) and, to our surprise, the reaction was almost completed within 5 min. Similar result was obtained with Co-1b<sub>red</sub> (76%, 90/10) (entry 3). In the case of Co-4, the trans-selectivity was same as that of Co-1<sub>red</sub>, whereas the yield was low (31%, 92/8) (entry 4).<sup>10</sup> Co<sup>II</sup>-TPP showed the lesser catalytic activity as well as trans-selectivity under the same conditions (6%, 72/28) (entry 5). Furthermore, the catalytic reaction of Co-1<sub>red</sub> proceeded even with 0.1 mol% of **Co-1a**<sub>red</sub> (TON = 390, entry 6). Notably, **Co-1**<sub>red</sub> showed an excellence catalytic activity and stability under the air, whereas the cyclopropanation reaction of olefins with EDA is usually carried out under anaerobic condition. Particularly, the rate of reaction was dramatically increased compared with Co-4 and Co"-TPP.

The attempt to clarify the structure of the initially reduced species (**Co-1a**<sub>red</sub>), which we assume the nitrite-free **Co<sup>II</sup>-1a**, is so far unsuccessful. The mass spectra indicated at least the thiopyridine group was retained in the catalyst during the catalytic reaction. We believe the coordinated thiopyridine ligand tethered to the NCP skeleton affects the catalytic ability through electron-donation to the metal center and protects the inner carbon, which is rather reactive in an sp<sup>2</sup> form of the ordinary NCP metal complexes.<sup>17</sup>

#### Conclusions

In summary, the bioinspired pentadentate NCP ligand 1 and its metal complexes Ru(CO)-1 and  $Co(NO_2)-1$  were synthesized with simple procedures in good yields, and the structures were revealed by X-ray analysis.  $Co-1_{red}$  exhibited an excellent catalytic activity, especially, a large acceleration in the cyclopropanation reaction of styrene with EDA. Because of the facile synthesis and good stability and its intrinsic nature to stabilize higher oxidation states of metals, it appears that the present bioinspired pentadentate NCP ligand would provide an ideal platform for the metal catalysts in a variety of reactions.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** N-confused porphyrin • pentadentate • catalyst •cyclopropanation• acceleration effect

- Review see, a) B. Meunier, S. P. P. de Visser, S. Shaik, *Chem. Rev.* 2004, 104, 3947–3980; b) D. Mansuy, *C. R. Chimie* 2007, 10, 392–413; c) A. Lombardi, F. Nastri, V. Pavone, *Chem. Rev.* 2001, 101, 3165–3190; d) R. Fasan, *ACS Catal.* 2012, 2, 647–666.
- a) J. T. Groves, T. E. Nemo, R. S. Meyers, J. Am. Chem. Soc. 1979, 101, 1032–1033;
  b) E. T. Farinas, M. Alcalde, F. Arnold, Tetrahedron 2004, 60, 525–528; c) K. L. Tee, U. Schwaneberg, Angew. Chem. Int. Ed. 2006, 45, 5380–5383; Angew. Chem. 2006, 118, 5507–5509; d) A. Li, J. Liu, S. Q. Pham, Z. Li, Chem. Commun. 2013, 49, 11572–11574.
- [3] a) Handbook of Porphyrin Science, Vol. 21 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard) World Scientific, Singapore, 2012; b) R. A. Decréau, in Handbook of Porphyrin Science, Vol. 22, (Eds.: K. M. Kadish, K. M. Smith, R. Guilard); World Scientific, Singapore, 2012, 235–305; c) J. C. Barona-Castaño, C. C. Carmona-Vargas, T. J. Brocksom, K. T. de Oliveira, Molecules 2016, 21, 310.
- [4] a) H. Furuta, T. Asano, T. Ogawa, J. Am. Chem. Soc. 1994, 116, 767–768; b) P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, T. Głowiak, Angew. Chem. Int. Ed. Engl. 1994, 33, 779–781; Angew. Chem. 1994, 106, 805–808.
- a) H. Furuta, T. Ogawa, Y. Uwatoko, K. Araki, *Inorg. Chem.* 1999, *38*, 2676–2682; b) H. Maeda, Y. Ishikawa, T. Matsuda, A. Osuka, H. Furuta, *J. Am. Chem. Soc.* 2003, *125*, 11822–11823.
- [6] T. Niino, M. Toganoh, B. Andrioletti, H. Furuta, Chem. Commun. 2006, 4335–4337.
- [7] T. Yamamoto, M. Toganoh, H. Furuta, *Dalton Trans.* 2012, 41, 9154– 9157.
- [8] Only a few examples of 3H'-forms have been reported. See, a) I. Schmidt, P. Chmielewski, Z. Ciunik, J. Org. Chem. 2002, 67, 8917–8927; b) I. Schmidt, P. Chmielewski, J. Inorg. Chem. 2003, 42, 5579–5593; c) C.-H. Hung, W.-M. Ching, G.-F. Chang, C.-H. Chuang, H.-W. Chu, W.-Z. Lee, Inorg. Chem. 2007, 46, 10941–10943; d) H.-W. Jiang, Q.-Y. Chen, J.-C. Xiao, Y.-C. Gu, Chem. Commun. 2009, 3732–3734; e) N. Grzegorzek, L. Latos-Grażyński, L. Szterenberg, Org. Biomol. Chem. 2012, 10, 8064–8075; f) Y.-C. Wang, J.-H. Chen, S.-S. Wang, J.-Y. Tung, Inorg. Chem. 2013, 52, 10711–10713; g) N. Grzegorzek, E. Nojman, L. Szterenberg, L. Latos-Grażyński, Inorg. Chem. 2013, 52, 2599–2606; h) C.-C. Chiu, J.-H. Chen, S.-S. Wang, J.-Y. Tung, Polyhedron 2014, 83, 212–219; i) C.-H. Chuang, W.-F. Liaw, C.-H. Hung, Angew. Chem. Int. Ed. 2016, 55, 5190–5194; Angew. Chem. 2016, 128, 5276–5280.
- [9] Similar pentadentate tetrapyrrolic ligands bearing a 2-picolyl group in a corrole framework were synthesized via *N*-alkylation. Z. Gross, N. Galili, *Angew. Chem. Int. Ed.* **1999**, 38, 2366–2369; *Angew. Chem.* **1999**, *111*, 2536–2540.
- [10] Catalytic cyclopropanation of styrene with EDA using cobalt NCPs was investigated previously. Co-4 (1.0 mol%) was reported to show the catalytic activity (86%, 93:7) at room temperature for 20 h under nitrogen atmosphere. K. B. Fields, J. T. Engle, S. Sripothongnak, C. Kim, X. P. Zhang, C. J. Ziegler, *Chem. Commun.* 2010, 47, 749–751.
- [11] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1579795 (1a), CCDC 1579796 (Co(NO<sub>2</sub>)-1b), CCDC 1579797 (Ru(CO)-1a) and CCDC 1579798 (Ru(CO)-3a)) and data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.
- [12] R. G. Little, J. A. Ibers, J. Am. Chem. Soc. 1973, 95, 8583–8590.
- [13] Under the reaction conditions, the nitrate ion of cobalt salt could be reduced to the nitrite. The FTIR spectrum of **Co(NO<sub>2</sub>)-1a** showed the typical stretching mode of nitrite anion ( $\nu_{NO}$ ; 1311, 1405 cm<sup>-1</sup>). T. S. Kurtikyan, S. R. Eksuzyan, J. A. Goodwin, G. S. Hovhannisyan, *Inorg. Chem.* **2013**, *52*, 12046–12056.

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- [14] S. O. Obare, T. Ito, G. J. Meyer, Environ. Sci. Technol. 2005, 39, 6266– 6272.
- [15] Review see, a) D. Intrieri, D. M. Carminati, E. Gallo, *Dalton Trans.* 2016, 45, 15746–15761; b) S. M. Ujwaldev, K. S. Sindhu, A. P. Thankachan, G. A. Anilkumar, *Tetrahedron* 2016, 72, 6175–6190; c) C.-M. Che, J.-S. Huang, *Chem. Commun.* 2009, 3996–4015; d) D. Chatterjee, *Coord. Chem. Rev.* 2008, 252, 176–198.
- [16] Review see, a) D. Intrieri, A. Caselli, E. Gallo, *Eur. J. Inorg. Chem.* 2011, 5071–5081; b) S. Zhu, X. Cui, X. P. Zhang, *Eur. J. Inorg. Chem.* 2012, 430–434.
- [17] M. Toganoh, H. Furuta, In *Handbook of Porphyrin Science, Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard) World Scientific, Singapore, **2010**, 295–362.

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