

# N - Confused Porphyrin - aza - Dipyrin Chimera: A Versatile Metal Coordination Ligand Using its Unique NH Tautomerism

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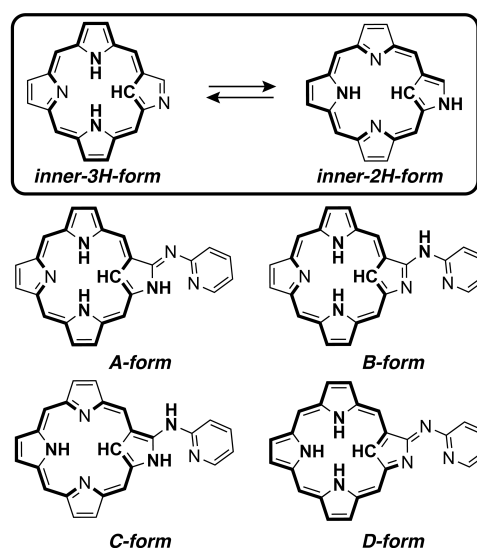
# N-Confused Porphyrin-aza-Dipyrin Chimera: A Versatile Metal Coordination Ligand Using its Unique NH Tautomerism

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**Abstract:** A novel N-confused porphyrin (NCP) analogue bearing an external aza-dipyrin-like coordination site was synthesized by a Schiff-base forming reaction of N-confused oxoporphyrin and 2-aminopyridine derivatives. The chimera molecule enhances the intrinsic NH tautomerism of NCP to enable four possible tautomeric structures, three of which were identified by metal coordination.

As represented by heme in blood<sup>[1]</sup> and chlorophyll in plants,<sup>[2]</sup> porphyrin, a naturally-occurring aromatic macrocycle consisting of alternately arranged four pyrrole rings and four bridging methine carbon atoms, is a versatile ligand for transition metal ions and main group elements.<sup>[3]</sup> These metalloporphyrins have been extensively studied due to their potential application in a variety of research fields. Since the divalent tetradentate inner core of porphyrin plays a crucial role in its unique coordination chemistry, much effort has been devoted to develop coordination properties by structural modification according to the synthetic protocols such as isomerization, contraction, and expansion.<sup>[4]</sup> Among these kinds of structurally-modified porphyrin analogues, N-confused porphyrin (NCP),<sup>[5,6]</sup> one of the isomeric porphyrins, in which one pyrrole ring in the structure of porphyrin is inverted and bridged at the  $\alpha$ - and  $\beta$ -positions, draws a sharp contrast from other porphyrin analogues with its unique coordination properties. Owing to the NH tautomerism between the inner nitrogen atoms of the regularly arranged pyrrole rings and the outer nitrogen atom of the inverted pyrrole ring (so-called 'confused pyrrole ring'), NCP can take two tautomeric structures, namely, **inner-2H-form** and **inner-3H-form** (Figure 1), which enable NCP to coordinate both divalent (+2) and trivalent (+3) metal ions.<sup>[7,8]</sup> In addition, the confused pyrrole ring can also function as an outer coordination site to create metal-coordinated dimers and trimers.<sup>[7,9-11]</sup> By introducing a hydrogen-bonding site to the confused pyrrole ring, the intrinsic NH tautomeric behavior of NCP can be linked to dynamic behaviors. Recently, our group reported that the

extended NCP derivative with a pyridylethenyl group exhibited *cis-trans* isomerization of the ethenyl moiety, which proceeded in a concerted manner with the NH tautomerism, along with marked changes in both absorption and emission properties.<sup>[12]</sup> In order to further utilize the NH tautomerism of NCP towards creation of novel metal coordination properties, we, herein, designed a chimera molecule, in which an aza-dipyrin-like structure is half-embedded in the structure of NCP. In this molecule, the aza-dipyrin-like moiety can serve not only as an outer coordination site, but also as a proton acceptor site. The target molecule was easily synthesized from N-confused oxoporphyrin<sup>[13]</sup> by a Schiff-base forming reaction of lactams and heteroaromatic amines, which we have recently developed for the synthesis of aza-BODIPY and its derivatives.<sup>[14]</sup> Four possible NH tautomers can be anticipated for this NCP-aza-dipyrin chimera structure, namely, **A~D-forms** as shown in Figure 1. **A-form** possesses three inner protons (2NH and 1CH) and one outer NH proton of the confused pyrrole ring, whereas in the structure of **B-form**, the outer proton of **A-form** is shifted to the *meso*-nitrogen atom of the aza-dipyrin-like moiety. **C-form** takes an inner-2H and outer-2H tautomeric form, in which one of the inner NH protons of **B-form** is transferred to the outer moiety. On the other hand, in the structure of **D-form**, the outer NH proton of **A-form** moves to the inner core to create an inner-4H and outer-0H tautomeric structure. Among the possible forms (**A~D**) above, three tautomeric structures were successfully realized by complexation of a boron difluoride (BF<sub>2</sub>) unit and Ag<sup>III</sup>, Ni<sup>II</sup>, and Re<sup>I</sup> ions.

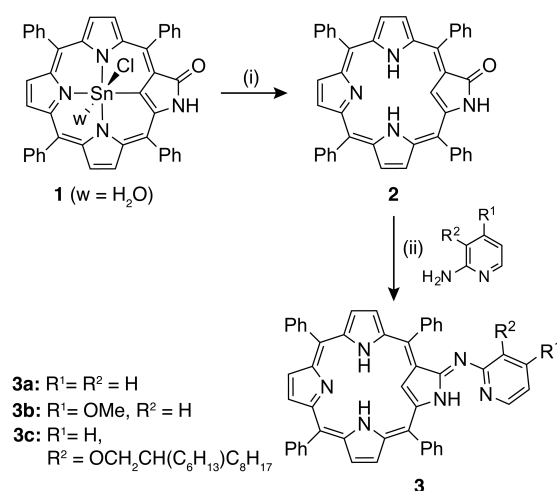


**Figure 1.** Inner-2H-form and inner-3H-form of NCP and four possible tautomers of NCP-aza-dipyrin chimera (**A~D-forms**).

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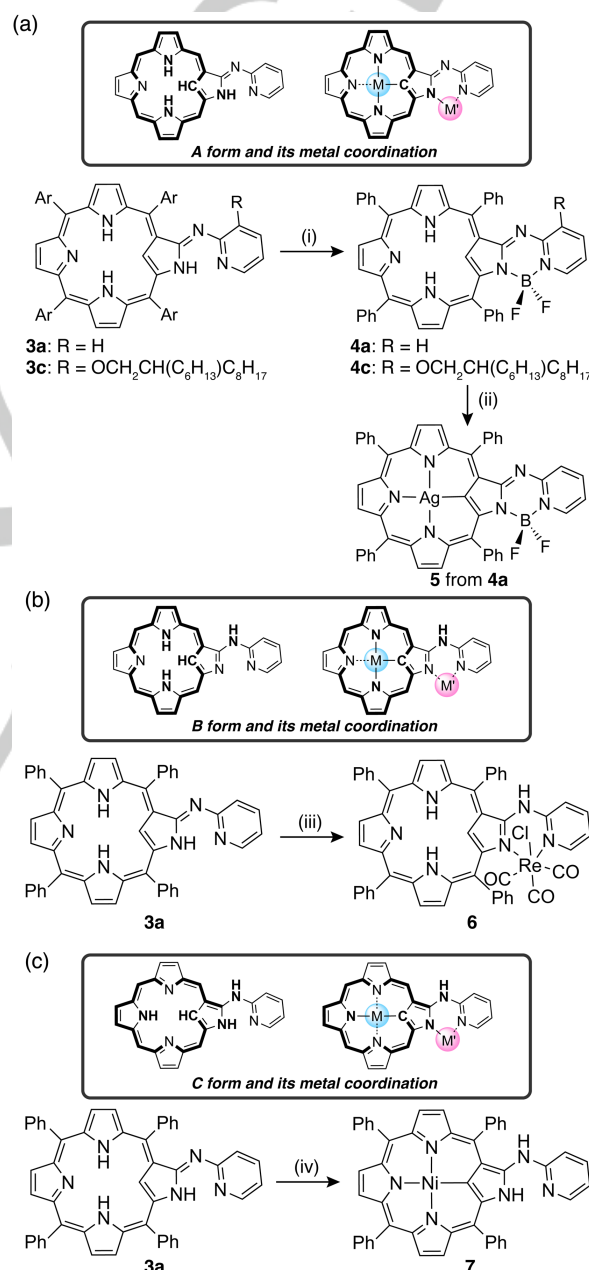
A free base form of N-confused oxoporphyrin (**2**) was synthesized by demetalation of its tin complex (**1**)<sup>[13]</sup> under acidic conditions. **2** was, then, converted into the NCP-aza-dipyrin chimera molecule (**3**) by a Schiff-base forming reaction with 2-aminopyridine derivatives in the presence of titanium tetrachloride (TiCl<sub>4</sub>) and triethylamine under refluxing conditions in toluene (Scheme 1).<sup>[14]</sup> **3** was characterized by the high-resolution mass spectrometry and <sup>1</sup>H NMR spectroscopy (see the Supporting Information (SI)). In the <sup>1</sup>H NMR spectrum of **3a**, the outer NH and inner CH protons of the confused pyrrole ring appear at  $\delta$  = 13.5 and –4.85 ppm, respectively. The inner NH protons were not observed at room temperature due to the rapid inner NH tautomerism.<sup>[15]</sup> The single crystal X-ray diffraction analysis confirmed the structure of **3b** as **A-form** (Figure 2a). Similar to **inner-3H-form** of conventional NCP, the confused pyrrole ring and aza-dipyrin-like moiety is tilted by ca. 30° from the rest part of the NCP structure due to the steric repulsion between the two NHs and one CH of the pyrrole rings in the core. Unlike regular aza-dipyrins, in which the nitrogen atoms point the same direction to form a hydrogen bond, the pyridine ring of **3b** is arranged in the opposite direction probably due to the packing force arising from the methoxy substituent.



**Scheme 1.** Synthesis of NCP-aza-dipyrin chimera **3**. Reaction conditions: (i) HCl/CH<sub>2</sub>Cl<sub>2</sub>, (ii) TiCl<sub>4</sub>, NEt<sub>3</sub>/toluene, reflux, N<sub>2</sub>.

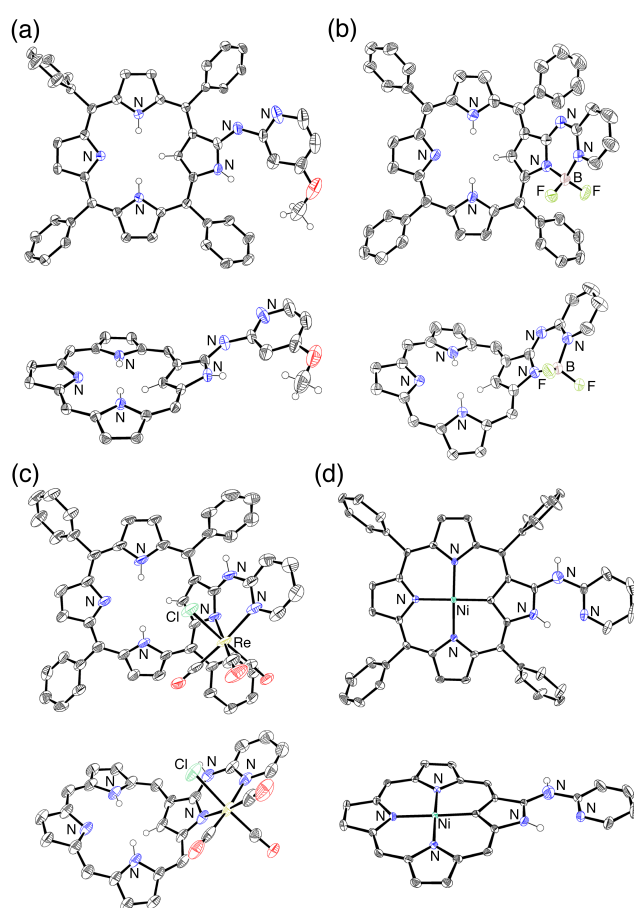
In **A-form**, the inner cavity and the outer aza-dipyrin-like moiety can function as trivalent tetradentate and monovalent bidentate ligands, respectively. These unique coordination properties were confirmed by BF<sub>2</sub> complexation (**4** in Scheme 2a), followed by silver metalation (**5** from **4a** in Scheme 2a). Despite the large dihedral angle of 59° between the NCP core and the aza-dipyrin-like moiety due to the steric hindrance of the branched alkoxy chain and the BF<sub>2</sub> unit, the ligand structure of the boron complex **4** is broadly similar to that of **3** (Figure 2b). This indicates that both **4** and **5** take **A-form**. Coordination of a Ag<sup>III</sup> ion in the core of **5** was confirmed by disappearance of the inner CH proton signal of **4a** at  $\delta$  = –4.66 ppm upon silver metalation (see the SI). As a next step, in order to examine the coordination property of aza-dipyrin-like moiety as a bidentate ligand, Re<sup>I</sup> metalation of **3a** using Re(CO)<sub>5</sub>Cl was investigated (Scheme 2b).

Judging from the disappearance of NH proton of **3a** at  $\delta$  = 13.5 ppm upon metalation, it is suggested that coordination of a rhenium ion took place at the aza-dipyrin-like moiety. The X-ray diffraction analysis unambiguously elucidated the structure of **6** (Figure 2c). The rhenium atom is coordinated in an octahedral fashion with three carbonyl groups and one chloride atom in addition to the aza-dipyrin ligand. The Re–Cl bond length of 2.4920(13) Å is within a typical Re<sup>I</sup>–Cl bond length. To our surprise, this indicates that the aza-dipyrin-like moiety does not



**Scheme 2.** Metal complexation of NCP-aza-dipyrin chimera **3**. Reaction conditions: (i) BF<sub>3</sub>·OEt<sub>2</sub>, NEt<sub>3</sub>/toluene, reflux, (ii) CF<sub>3</sub>CO<sub>2</sub>Ag/CH<sub>2</sub>Cl<sub>2</sub>, MeOH, r.t., (iii) Re(CO)<sub>5</sub>Cl, tBuOK/toluene, 50 °C, (iv) NiCl<sub>2</sub>·6H<sub>2</sub>O, tBuOK/CHCl<sub>3</sub>, EtOH, reflux.

function as a conventional monovalent bidentate ligand, but as an unusual zero-valent bidentate ligand. The NH tautomerism of this chimera molecule allows this type of coordination by taking **B-form**, in which NH proton of the confused pyrrole ring is shifted to the bridging nitrogen atom of the aza-dipyrin-like moiety (Figure 1). The proton transfer observed upon Re metalation of **3a** implied that the NCP core of **3** can function not only a trivalent ligand like **inner-3H-form** of normal NCPs, but also **inner-2H-form** as depicted as **C-form** in Figure 1. Such ligand property of **3** was, then, tested by metalation of Ni<sup>II</sup> ion (Scheme 2c). The <sup>1</sup>H NMR spectrum of **7** exhibited two NH protons at  $\delta$  = 13.7 and 7.51 ppm, which can be assigned as the confused pyrrolic NH proton and the bridging *meso*-NH proton of the aza-dipyrin-like moiety, respectively (see the SI). In the crystal structure of **7**, a Ni<sup>II</sup> atom is coordinated in a square planar fashion in the core of the NCP moiety, whereas the aza-dipyrin-like moiety possess two NH hydrogen atoms (Figure 2d). This crystal structure is in good agreement with the <sup>1</sup>H NMR spectrum of **7**. Unlike the free base form (**3**) and other complexes (**4** and **6**), **7** takes a planar structure due to the absence of steric repulsion caused by the inner NH and CH atoms.

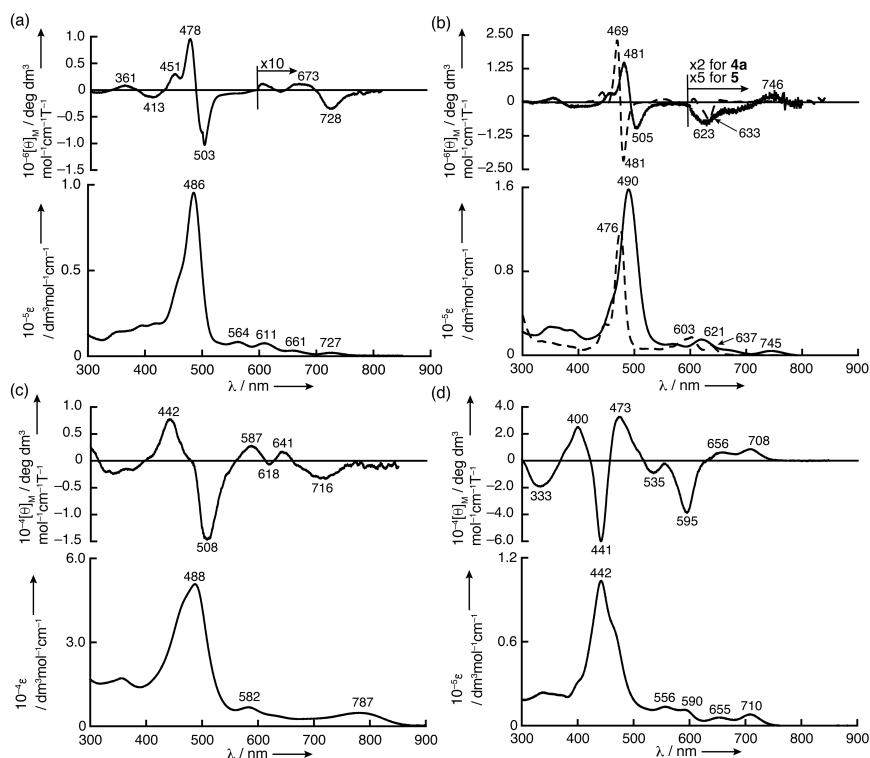


**Figure 2.** X-ray single crystal structures of (a) **3b**, (b) **4c**, (c) **6**, and (d) **7**, top view (top) and side view (bottom). The thermal ellipsoids are scaled to the 50% probability. Hydrogen atoms except for the NH and CH of pyrrole rings and the NH at the *meso*-position of aza-dipyrin-like moiety were omitted for clarity. The alkoxy substituent of **4c** in both views and *meso*-phenyl substituents in the side views were also omitted for clarity.

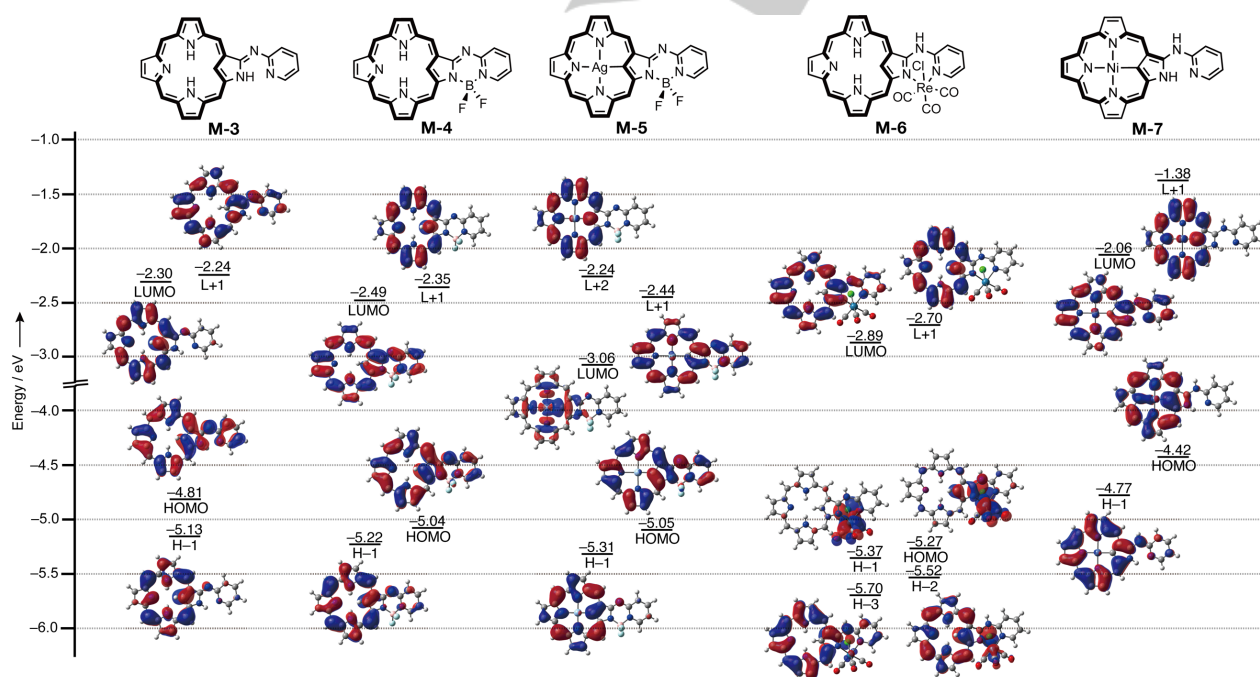
In order to reveal the impact of the NH tautomerism on the electronic structures, the UV/Vis/NIR absorption and magnetic circular dichroism (MCD)<sup>[16,17]</sup> spectra were measured in CHCl<sub>3</sub> (Figure 3), and the MCD sign sequence in the Q band regions was investigated with the help of the time-dependent density functional theory (TDDFT) calculations using model structures (**M-3~M-7**), in which phenyl substituents at the *meso*-positions are replaced with hydrogen atoms for simplicity (Figure 4 and Table S2 in the SI). Both the free base form **3a** and the BF<sub>2</sub> complex **4a** exhibit a sharp Soret band at around 490 nm and four weak Q bands from 550 nm to 750 nm, reflecting the same tautomeric structure of **A-form**. These absorption spectral features are also similar to that of **inner-3H-form** of NCP,<sup>[18]</sup> indicating that **A-form** takes porphyrin-like 18 $\pi$ -macrocyclic conjugation, which is highlighted with bold bond lines in Figure 1, as a main conjugation pathway. Upon Ag<sup>III</sup> metalation of **4a** to form **5**, the Soret band becomes sharp and blue-shifted, while the lowest-energy Q band absorption significantly shifts to the blue from 745 nm to 637 nm, probably due to structural rigidification by metal coordination inside the NCP core. Similar spectral changes were observed in the case of Ag<sup>III</sup> metalation of NCP.<sup>[19,20]</sup> Upon Re<sup>I</sup> metalation, both the Soret and Q bands of **6** become broader compared with **3a** and **4a** mainly due to the contribution of metal-to-ligand charge transfer transitions (MLCT). The Ni<sup>II</sup> complex (**7**) exhibits a slightly different absorption spectral profile as featured by the blue-shifted Soret band with a shoulder absorption. Considering that the nickel complex of NCP also shows similar absorption spectral changes from that of NCP,<sup>[6]</sup> the main conjugation of **C-form** is a cross-conjugated system like **inner-2H-form** of NCP (Figure 1).

Due to the absence of three-fold or higher molecular symmetries, the MCD signals observed for all the compounds in the Soret and Q band regions are assigned as Faraday *B* terms.<sup>[16]</sup> The sign sequence of the coupled oppositely signed Faraday *B* terms has correlation with relative magnitude differences between  $\Delta$ HOMO and  $\Delta$ LUMO, which denote energy gaps between the HOMO and HOMO–1 and between the LUMO and LUMO+1, respectively, according to Michl's terminology.<sup>[21]</sup> A minus-to-plus sign sequence in ascending energy is indicative of  $\Delta$ HOMO >  $\Delta$ LUMO, whereas a plus-to-minus sign sequence is observed when  $\Delta$ LUMO is greater than  $\Delta$ HOMO. In the cases of the free base **3a**, BF<sub>2</sub>-Ag<sup>I</sup> complex **5**, and Re<sup>I</sup> complex **6**, larger  $\Delta$ HOMO than  $\Delta$ LUMO is anticipated because a trough and peak are observed in the Q band region (**3a**: 728 and 673 nm, **5**: 633 and 606 nm, **6**: 716 and 641 nm). On the other hand, the BF<sub>2</sub> complex **4a** and Ni<sup>II</sup> complex **7** exhibit the opposite MCD sign sequence in ascending energy (**4a**: 746 and 623 nm, **7**: 708 and 595 nm). These plus-to-minus MCD spectra in the Q band region reflect  $\Delta$ HOMO <  $\Delta$ LUMO relationship. The TDDFT calculations and the frontier molecular orbital diagrams reproduced magnitude relationship between  $\Delta$ HOMO and  $\Delta$ LUMO in the cases of **3** and **7**;  $\Delta$ HOMO (0.32 eV) >  $\Delta$ LUMO (0.06 eV) for **M-3** and  $\Delta$ HOMO (0.35 eV) <  $\Delta$ LUMO (0.68 eV) for **M-7**. It is known that when  $\Delta$ HOMO and  $\Delta$ LUMO are close in energy, an MCD sign sequence becomes complex. That is the case for **4a**, whose  $\Delta$ HOMO and  $\Delta$ LUMO are 0.18 and 0.14 eV, respectively. In the case of **M-5**, a metal-centered orbital lies as a LUMO. Therefore,  $\Delta$ LUMO is estimated using the energies of the LUMO+1 and LUMO+2,





**Figure 3.** UV/Vis/NIR absorption (bottom) and MCD (top) spectra of (a) **3a**, (b) **4a** (solid line), **5** (dashed line), (c) **6**, and (d) **7** in  $\text{CHCl}_3$ .



**Figure 4.** Partial frontier molecular orbitals of model compounds of **3** (**M-3**), **4** (**M-4**), **5** (**M-5**), **6** (**M-6**), and **7** (**M-7**) derived from DFT calculations at the level of B3LYP/SDD for Re, LANL2DZ for Ag and Ni, and 6-31G(d) for the rest. H and L denote the HOMO and LUMO, respectively. The model structures used for the calculations are shown above.

which are delocalized on the NCP moiety with similar nodal patterns to the LUMO and LUMO+1 of **M-3**, **M-4**, and **M-7**. The  $\Delta\text{HOMO}$  (0.26 eV) >  $\Delta\text{LUMO}$  (0.20 eV) relationship of **M-5**

supports the minus-to-plus MCD sign sequence. The TDDFT calculation on **M-6** clearly revealed a significantly large contribution of MLCT transitions to the UV/Vis/NIR absorption

spectrum of **6**. The HOMO and HOMO–1 are localized on the rhenium-dipyrrin complex moiety. Therefore,  $\Delta$ HOMO is estimated from the next highest occupied molecular orbitals (HOMO–2 and HOMO–3). Although the  $\Delta$ HOMO >  $\Delta$ LUMO relationship inferred from the MCD sign sequence of **6** in the Q band region is not well reproduced ( $\Delta$ HOMO = 0.18 eV and  $\Delta$ LUMO = 0.19 eV calculated for **M-6**), this can be explained in terms of significant contribution of MLCT transitions, which may make assignment of absorption bands rather difficult.

In summary, NCP-aza-dipyrrin chimera was successfully synthesized using a Schiff-base forming reaction of N-confused oxoporphyrin and 2-aminopyridine derivatives. By extending the conjugated system of NCP through the aza-dipyrrin-like structure, this chimera molecule can take four NH tautomeric structures. Among them, three NH tautomeric forms were isolated as stable complexes. As is shown in the case of  $\text{BF}_2\text{-Ag}^{\text{I}}$  complex **5**, two different kinds of metal ions can be coordinated inside the NCP core and by the aza-dipyrrin-like moiety, and the oxidation states of the coordinated metal ions are mutually affected. In addition, metal ions with high oxidation states can be stabilized by the coordination in the structures of **A-**, **B-**, and **D-forms**. Although **D-form** has not yet been realized, this tautomer can coordinate metal ions with a +4 oxidation state. Isolation of **D-form** is currently being pursued. Combining mutually affected two metal centers and stabilization of high oxidation states, NCP-aza-dipyrrin chimera can be utilized as a unique ‘chameleon’ ligand for catalysts. Such possibility is also intensively being investigated in our laboratory.

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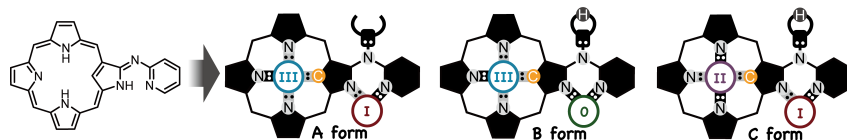
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## COMMUNICATION



A novel N-confused porphyrin (NCP) analogue bearing an external aza-dipyrrin-like coordination site was synthesized by a Schiff-base forming reaction of N-confused oxoporphyrin and 2-aminopyridine derivatives. The structure of this chimera molecule enhances the intrinsic NH tautomerism of NCP to enable four possible tautomeric structures, three of which were identified by metal coordination.

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**N-Confused Porphyrin-aza-Dipyrrin  
Chimera: A Versatile Metal  
Coordination Ligand Using its Unique  
NH Tautomerism**