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N-Confused Double-Decker Porphyrins

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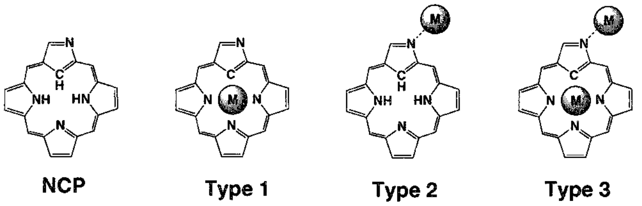
Porphyrin assembly by metal coordination is one of the facile strategies to develop potent optical and electronic materials.[1,2] For such studies, coordinating ligands like pyridine and imidazole have been widely used for bridging. However, there are few, if any, reports on the formation of a metal-coordination-assisted porphyrin dimer or oligomer directly linked at the pyrrolic peripheral, where the strong interaction of the mutual π-electrons could be anticipated.[2,3] "N-Confused porphyrin" (NCP, Chart 1) is a porphyrin isomer in which one of the pyrrolic rings is inverted.[4] Similarly to the normal porphyrins, NCP can coordinate a metal in the porphyrin core by using the inner carbon and nitrogens (type 1).[4b,5,6] Owing to the outward pointing nitrogen, outer-N coordination is also conceivable (type 2). If the metals bind in both ways, bimetallic species would be formed (type 3). Especially, in the outer-N coordination cases, the metal-bridged dimer and polymer could be derived if the doubly N-confused porphyrins[6b] are used. In this communication, two types of palladium−NCP complexes, inner-coordinated Pd(II)−NCP (**1**) and inner- and outer-N-coordinated, double-decker Pd complexes,[7] (Pd(II)−NCP)$_2$ (**2a**,**b**), are reported. To the best our knowledge, the latter Pd dimers are the first examples of the outer-N coordination in the NCP family.

Chart 1



Complexation of Pd with NCP was studied using N-confused tetratolylporphyrin (NCTTP) and Pd(OAc)$_2$ in the two different solvent systems, CHCl$_3$ and toluene. First, the reaction was performed in CHCl$_3$ under reflux. After stirring for 0.5 h, a yellow-greenish Pd complex (**1**) was formed in 50% yield (Scheme 1). No other identifiable products were obtained. The optical absorption spectrum showed a broadened Soret band at 446 nm and five absorption peaks in the Q-band region from 532 to 766 nm in CHCl$_3$ (Supporting Figure 1a, Supporting Information). These spectral features are in marked contrast to that of a normal Pd(II)−TTP complex, where the Soret band is observed at 416 nm and the Q-band appears with two peaks at 523 and 554 nm. The ^{1}H NMR spectrum of **1** in CDCl$_3$ showed a signal at 9.95 ppm ascribable to the outer NH resonance, while the absence of inner NH and CH signals indicated metal coordination of type 1.

Direct evidence of the structure of **1** was obtained from X-ray single-crystal analysis (Figure 1a).[8] Pd metal was located in the middle of the porphyrin plane in a square-planar fashion. The average distances of Pd−N and Pd−C are 2.09 and 2.00 Å, which are comparable to those of Pd−N in the nearly square-planar Pd(II)−TPP (2.009 Å)[9] and Pd(II)−C σ-bond (2.00−2.05 Å).[10]

Next, the solvent was changed from CHCl$_3$ to toluene, and the solution was refluxed for 1 h. Two red-colored products (**2a** and **2b**) along with NCTTP−Pd (**1**) were isolated in yields of 27%, 36%, and 19%, respectively (Scheme 1). The FABMS spectra of both **2a** and **2b** showed the parent peaks at 1550 au in line with the corresponding dimeric species, (Pd−NCTTP)$_2$. The Soret and Q-bands of both complexes are red-shifted and broadened compared to those of the monomeric Pd complex **1** (Supporting Figure 1b, Supporting Information), which suggested the significant distortion of the porphyrin rings in **2a** and **2b**. In CDCl$_3$, a set of inner protons (CH, NH) was observed at (−4.40, 0.09) ppm in **2a**, while two sets of signals were seen in **2b** at (−3.83, 0.04) and (−3.28, 0.51) ppm, presumably reflecting the symmetrical and unsymmetrical structures of **2a** and **2b**, respectively.

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(8) Crystallographic data for **1**: $C_{48}H_{36}N_4Pd$, $T = 296$ K, MW = 775.24, violet, monoclinic, $P2_1/n$, $a = 9.753(2)$ Å, $b = 9.228(2)$ Å, $c = 21.184(2)$ Å, $\beta = 98.61(1)°$, $V = 1885.1(5)$ Å^3, $D_c = 1.366$ g/cm^3, $Z = 2$, $R = 0.047$, $R_w = 0.046$, GOF = 1.400. There is a center of symmetry at the center of the macrocycle; hence the inner C and N atoms are disordered and not distinguishable in the X-ray structure.

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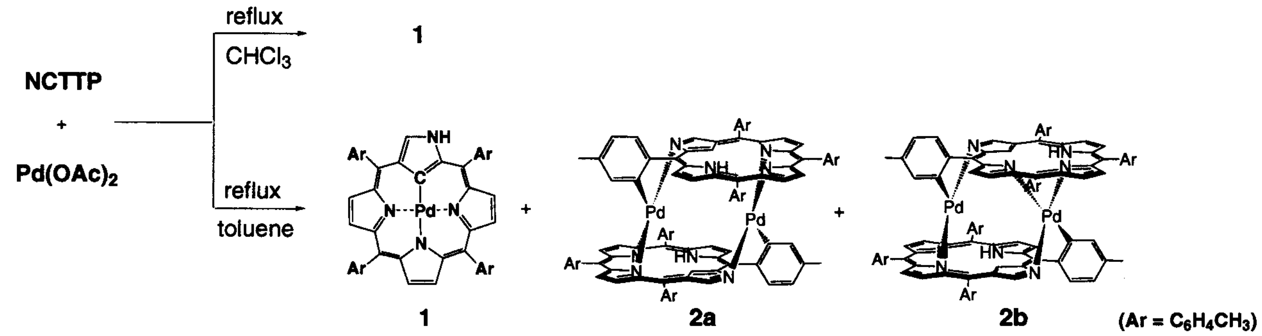
Scheme 1



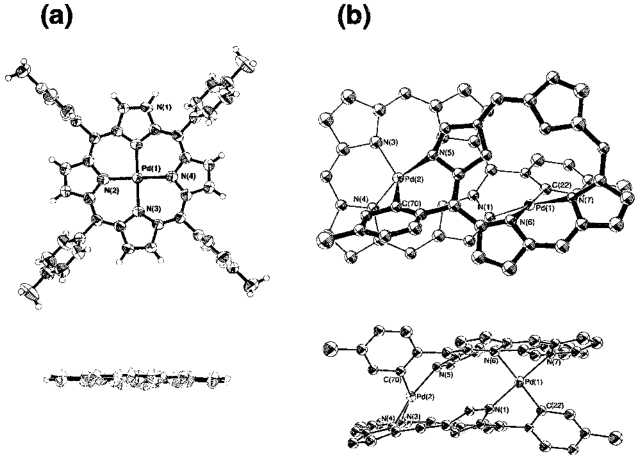


Figure 1. Molecular structures of (a) Pd(II)−NCTTP (**1**) and (b) (Pd(II)−NCTTP)$_2$ (**2b**). For clarity, uncoordinated tolyl groups are omitted in part b. Selected bond lengths (Å) for **2b**: Pd(1)−N(1), 2.00(2); Pd(1)−N(6), 2.12(2); Pd(1)−N(7), 2.08(2); Pd(1)−C(22), 2.00(2); Pd(2)−N(3), 2.29(2); Pd(2)−N(4), 2.03(1); Pd(2)−N(5), 2.05(2); Pd(2)−C(70), 1.99(2). Selected angles (deg) for **2b**: N(1)−Pd(1)−C(22), 87.6(7); C(22)−Pd(1)−N(7), 95.3(7); N(6)−Pd(1)−N(7), 86.2(6); N(1)−Pd(1)−N(6), 91.1(6); N(3)−Pd(2)−N(4), 81.8(6); N(3)−Pd(2)−N(5), 107.3(6); N(4)−Pd(2)−C(70), 91.6(7); N(5)−Pd(2)−C(70), 86.1(7).

The explicit structure of **2b** was elucidated by single-crystal X-ray analysis.[11] Each Pd atom was tetracoordinated with the outer-N of the confused pyrrole, *o*-C of *meso*-tolyl, and two pyrrolic inner-N's of the other NCTTP, affording a slipped dimer of double-decker type (Figure 1b). Two Pd sites are nonequivalent, namely, the typical dihedral angles of Pd containing planes (ϕ_s) are 1.72° for $\angle\phi_{\mathrm{Pd-N6-N7}}\phi_{\mathrm{Pd-N7-C22}}$ with Pd(1) and −24.86° for $\angle\phi_{\mathrm{Pd-C70-N5}}\phi_{\mathrm{Pd-N5-N3}}$ with Pd(2) (Supporting Figure 2, Supporting Information). Thus, the geometry of Pd(1) is close to square-planar but Pd(2) is significantly distorted to tetrahedral. The Pd−C bond distances (Å) of both sites are almost the same: Pd(1)−C(22), 2.00; Pd(2)−C(70), 1.99(2). However, those of Pd−N differ largely: Pd(1)−N(1), 2.00(2); Pd(1)−N(6), 2.12(2); Pd(1)−N(7), 2.08 (2); Pd(2)−N(3), 2.29(2); Pd(2)−N(4), 2.03(1); Pd(2)−N(5), 2.05(2).

The obtained structure of **2b** can well explain the unsymmetrical ^{1}H NMR spectrum and, in turn, suggests the symmetrical structure of the other complex **2a**. At present, for the lack of the crystal structure of **2a**, the other isomeric structures which differ with respect to the coordinating nitrogens cannot be ruled out.[12] However, the observed transformation from **2a** to **2b** in triethylamine/CHCl$_3$ (v/v = 1/1) at reflux can be simply interpreted by the weak coordinating nature of the dipyrryl group to arouse the recombination of one of the Pd−N bonds in **2a**. Both **2a** and **2b** were stable under neutral conditions but decomposed instantly to the monomeric NCP in the presence of a small amount of TFA in CH$_2$Cl$_2$.

It is well-known that Pd(II) undergoes the facile palladation of aromatic compounds which have a substituent containing nitrogen at a position suitable for chelating.[13,14] Mechanistically, thus, the coordination of Pd(II) at outer-N and succeeding *o*-C palladation to the *meso*-tolyl group, yielding an outer-N Pd complex, might compete with the inner-N coordination. The latter would transform to the stable inner Pd complex, **1**. On the other hand, the resulting outer-N coordinating monomers would react with each other to give **2a** and **2b**, respectively. The transformation from **1** to **2a** or **2b** was not observed in the refluxing toluene. We believe that the square-planar Pd site formed initially could determine the geometry of the second Pd significantly, where the selective formation of **2a** and **2b** is induced. Here, the sacrifice of either the planarity of the porphyrin plane or the square-planar geometry of Pd is necessary to form **2a** or **2b**. Thus, N-confused double-decker porphyrins obtained seem to stand on the subtle balance between the planarity and the distortion.[15] The difference of the reaction mode in the two solvents could be ascribed to the activation energy for the *o*-C palladation which requires a high temperature as in refluxing toluene.[16]

In conclusion, we have prepared a new type of double-decker porphyrin using NCTTP and Pd(OAc)$_2$. The Pd coordination mode was unique in that inner- and outer-N as well as *o*-C were included. If the dimer **2a** (or **2b**) dissociates to monomers by adding the second metal for the chelation in the core, the coordination site of the Pd(II) would become available. Such bimetallic NCP monomers (type 3) are attractive for use as catalysts. Attempts to combine both inner and outer coordination in the NCP monomer are currently underway.

Supporting Information Available: Listings of synthetic procedures, spectral data, and absorption spectra for **1**, **2a**, and **2b**; dihedral angles of Pd-containing planes of **2b**; isomeric structures of **2a**; X-ray crystallographic files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data for **2b**: C$_{96}$H$_{72}$N$_8$Pd$_2$, T = 296 K, MW = 1550.48, red, triclinic, $P\bar{1}$, a = 16.929(1) Å, b = 22.7847(9) Å, c = 14.5877(5) Å, α = 95.559(3)°, β = 103.133(5)°, γ = 70.950(6)°, V = 5178.1(6) Å^3, D_c = 0.994 g/cm^3, Z = 2, R = 0.104, R_w = 0.152, GOF = 2.640.

(12) The possible isomeric structures are shown in the Supporting Information.

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