Rhenium Complexes of *N*-Methyl N-Confused Tetraphenylporphyrin and Its Normal Isomer

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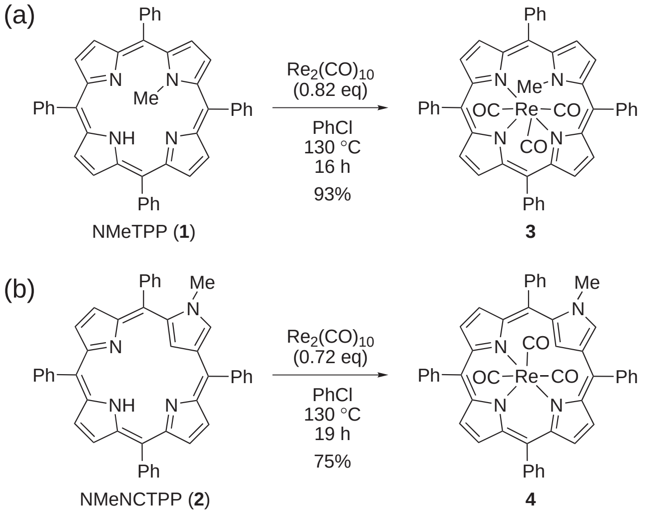
The rhenium tricarbonyl complexes bearing tridentate porphyrin ligands, *N*-methyltatraphenylporphyrin and *N*-methyl N-confused tatraphenylporphyrin, were prepared and their structures were studied by X-ray crystallographic analysis. Drastic change of HOMO–LUMO gap by *confusion* of *N*-methylpyrrole moiety was illustrated from experimental and theoretical studies.

Inversion or *confusion* of pyrrole rings within porphyrin macrocycles created a new area of research, and the field has expanded at an accelerating rate in the last decade.[1,2] Existence of peripheral nitrogen atoms made it possible to construct supramolecular structures,[3] new macrocyclic skeletons,[4] and switching functions.[5] While many efforts to construct metal complexes analogous to normal porphyrins have been exercised, there has been no report focusing on tripodal coordination using three inner nitrogen atoms of N-confused porphyrins.[6] This time we have investigated the rhenium complexes bearing *N*-methyltatraphenylporphyrin (NMeTPP)[7] and *N*-methyl N-confused tatraphenylporphyrin (NMeNCTPP)[8] ligands and revealed that remarkable change of HOMO–LUMO gap was induced by *confusion* of *N*-methylpyrrole ring.

Metallation of porphyrinoid ligands was achieved by the simple thermal reactions in a similar manner as the related compounds (Scheme 1).[9] Upon heating a PhCl solution of NMeTPP (**1**) with $Re_2(CO)_{10}$ at 130 °C for 16 h, oxidative metal coordination proceeded efficiently to give $Re(NMeTPP)(CO)_3$ (**3**) in 93% yield as purple crystals. Similarly, the reaction of NMeNCTPP (**2**) with $Re_2(CO)_{10}$ at 130 °C for 19 h afforded $Re(NMeNCTPP)(CO)_3$ (**4**) in 75% yield as green crystals. For both compounds, the mass, ^1H NMR, and ^{13}C NMR spectra were fully consisted with the assigned structures. For example, the singlet signal due to the methyl group of **3**, which placed within the macrocyclic ring, was observed at δ −4.76 ppm, indicating strong aromatic character of the normal porphyrin moiety. In contrast, the methyl group of **4** placed at the peripheral position and the signal appeared at δ 3.43 ppm. The signal due to the inner CH moiety of **4** appeared at δ −0.72 ppm, which suggested moderate aromatic character of the N-confused porphyrin macrocycle. While the complexes **3** and **4** were stable against air and sunlight even in solution at ambient temperature, they were immediately dematallated under acidic conditions to give the parent ligands **1** and **2**, respectively, in quantitative yields.

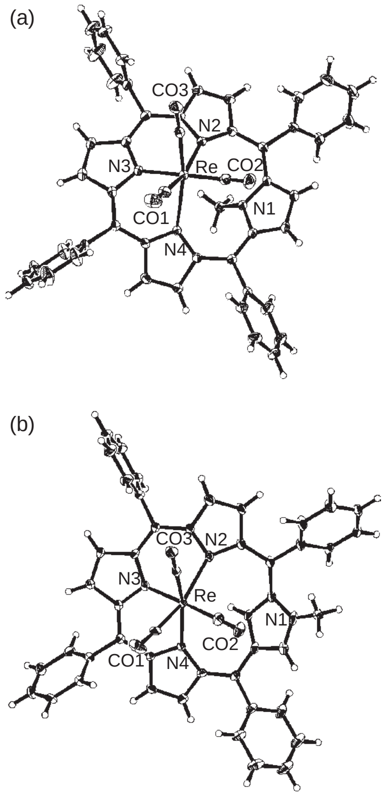


NMeTPP (**1**) **3**

NMeNCTPP (**2**) **4**

Scheme 1. Preparation of the rhenium(I) complexes of (a) normal porphyrin (**1**) and (b) N-confused porphyrin (**2**).

Details of molecular structures of **3** and **4** were elucidated by X-ray crystallographic analysis (Figure 1).[10] In both complexes, tripyrran moiety coordinated to the metal center in κ^3-fashion and the rhenium metal further has three carbonyl ligands. The



(a)

Re-N2	2.368(2)
Re-N3	2.150(2)
Re-N4	2.349(2)
Re-CO1	1.890(3)
Re-CO2	1.922(2)
Re-CO3	1.882(3)

(b)

Re-N2	2.364(4)
Re-N3	2.134(5)
Re-N4	2.383(5)
Re-CO1	1.907(7)
Re-CO2	1.926(8)
Re-CO3	1.836(7)

Figure 1. Molecular structures of (a) **3** and (b) **4** with 30% probability level ellipsoids. The solvent molecules are omitted for clarity. Selected bond lengths (Å) are also shown. Since the *N*-methyl moiety of **4** is disordered, one of the possible structures is shown.

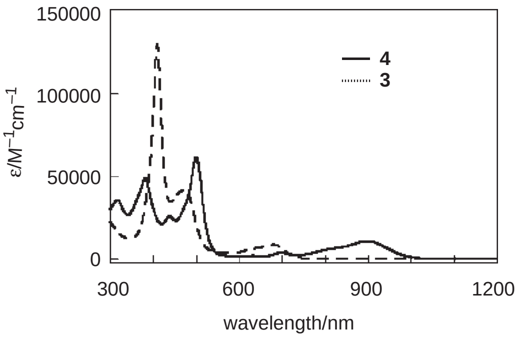


Figure 2. Absorption spectra of **3** and **4** in CH_2Cl_2.

Table 1. Oxidation and reduction potentials (V vs. Fc^+/Fc) of **3** and **4** obtained by cyclic voltammetry[a]

	M^+/M	M/M^-	M^-/M^{2-}	$M^+/M - M/M^-$
3	0.36	−1.64	−2.06	2.00
4	0.02	−1.46	−1.94	1.48

[a]Conditions: 0.1 M Bu_4NPF_6 in CH_2Cl_2 at 23 °C with a Pt working electrode. Scan rate = 100 mV/s.

rest pyrrole rings were tilted from porphyrin mean plane, consisting of 24 heavy atoms, in 16.6° for **3** and 20.9° for **4**, respectively, so as to avoid steric repulsion. The bond lengths around the metal center in **3** and **4** were nearly identical. Distinct difference between **3** and **4** is only junction between *N*-methylpyrrole and tripyrran unit, and hence comparison of **3** and **4** would be good probe for the effect of *confusion* of *N*-methylpyrrole moiety.

Absorption spectrum and electrochemical data were dramatically changed by *confusion* of *N*-methylpyrrole moiety. In absorption spectrum (Figure 2), the Soret band of **3** appeared at 410 nm with strong intensity. Contrastingly, the Soret-like band of **4** was split to two peaks at 382 nm and 501 nm. More remarkably, large red shift from 681 nm to 899 nm was observed in the longest maximum absorption wavelength. Electrochemical data also showed significant difference (Table 1). While one reversible oxidation wave (M^+/M) and two reversible reduction waves (M/M^- and M^-/M^{2-}) were observed for both **3** and **4**, the first oxidation potential of **4** was more negative in 0.34 V than that of **3** and the first reduction potential of **4** was more positive in 0.18 V than that of **3**. These results clearly represent narrow HOMO–LUMO gap of **4** and mean that it become easier to take electrons in and out by *confusion*, which was further supported by theoretical study.

Kohn–Sham orbitals of the model compounds for **3** and **4**, calculated at B3LYP/631LAN level, were shown in Figure 3.[11] While description of double bonds in Kekulé structures differs, whole shapes of HOMO and LUMO resemble each other. Nevertheless, higher HOMO level as well as lower LUMO level was obtained for the model compound of **4**, which was consisted with the spectral data.[12]

In conclusion, the metal complexes bearing κ^3-porphyrin ligands, $Re(NMeTPP)(CO)_3$ (**3**) and $Re(NMeNCTPP)(CO)_3$ (**4**) were synthesized by the oxidative metallation reactions. Comparison of **3** and **4** gave fundamental insight into the effect of *confusion* of *N*-methylpyrrole moiety. Especially, drastic change in HOMO–LUMO gap was caused by *confusion*. Further study to clarify the effect and application of *confusion* of *N*-substituted pyrrole ring is undergoing.

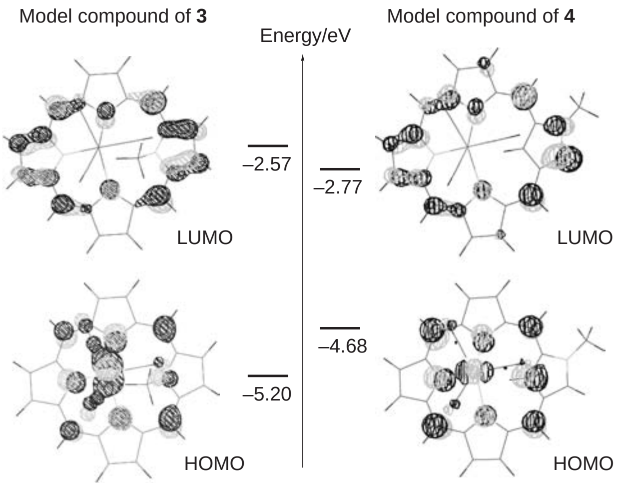


Figure 3. HOMO and LUMO of the model compounds for **3** and **4**.

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6 The reaction of N-confused porphyrin with $Re_2(CO)_{10}$ gave the N-fused porphyrin rhenium complex. For details, see ref. 9a.

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10 Crystal data: **3**, Violet prism, $C_{48}H_{31}N_4O_3Re$, $M_r = 898.00$, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.3952(7)$, $b = 14.7920(7)$, $c = 18.0256(9)$ Å, $\beta = 98.520(1)°$, $V = 3795.9(3)$ Å^3, $Z = 4$, $T = 223$ K, $R = 0.0290$ ($I > 2\sigma(I)$), $R_W = 0.0340$ (all data), GOF on $F^2 = 1.231$, CCDC reference number 270141; **4**, Green prism, $C_{49}H_{33}Cl_2N_4O_3Re$, $M_r = 982.89$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.3463(8)$, $b = 12.8810(9)$, $c = 14.4269(10)$ Å, $\alpha = 93.135(1)$, $\beta = 107.516(1)$, $\gamma = 108.516(1)°$, $V = 2045.9(2)$ Å^3, $Z = 2$, $T = 223$ K, $R = 0.0431$ ($I > 2\sigma(I)$), $R_W = 0.0985$ (all data), GOF on $F^2 = 0.912$, CCDC reference number 270142.

11 All the phenyl groups of **3** and **4** were replaced by the hydrogen atoms. LANL2DZ basis set was used for the rhenium atoms and 6-31G** basis set for the rest.

12 Since similar trend was also observed in comparison of **1** with **2**, the difference should originate in *confusion*.

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