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Synthesis and Properties of Acetylene-bridged N-Confused Porphyrin Dimers

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Acetylene-bridged N-confused porphyrin (NCP) dimers were synthesized by Stille coupling reactions. Moderate electronic interaction between the NCP chromophores was observed in the inner-3H tautomers while strong interaction was observed in the inner-2H tautomers.

Cross-coupling reactions are one of the most powerful methods to construct large π-conjugated molecules.[1] Among such molecules, porphyrin dimers as well as oligomers are a particularly important class of compounds, which often show fascinating electronic properties and functions, such as two-photon absorption, light-harvesting, and electron transport.[2]

N-Confused porphyrin (NCP)[3] is a uniquely interesting porphyrin analog, showing prominent functions in coordination chemistry, photochemistry, and structural organic chemistry.[4] One intrinsic characteristic of NCP is NH-tautomerization, which allows change of the electronic state significantly (Figure 1).[5] Thus, the inner-3H tautomer (NCP3H) has an [18]annulenic substructure and is strongly aromatic, while the inner-2H tautomer (NCP2H) loses the [18]annulenic substructure and is moderately aromatic.[6] Accordingly, NCP3H is thermodynamically more stable than NCP2H and much difference is found in their photophysical properties.[7] Previously, we have demonstrated that intramolecular energy transfer could be controlled by NH-tautomerization in the porphyrin–NCP dyad system.[8] Additionally, substitution effect at the 3-position would be much different between NCP3H and NCP2H.[9] Along the lines of these findings, we can expect interesting electronic structures in 3,3′-acetylene-bridged NCP dimers. In this paper, the synthesis and properties of 3,3′-acetylene-bridged NCP dimers by the Stille coupling are reported.

First, the reactions of 3-bromo-NCPs with tributyl(phenylethynyl)tin were studied to prepare 3-alkynyl-NCPs (Scheme 1). The alkynylated NCPs were previously prepared by the Sonogashira coupling[9] or inversion of alkynylated N-fused porphyrins.[10] The reaction of N-confused 3-bromotetraphenylporphyrinatosilver(III) complex **1** proceeded smoothly with $\mathrm{Pd(OAc)_2/AsPh_3}$ catalyst to give $\mathrm{Ag^{III}}$(NCP3H)–CC–Ph **2** in 63% yield. Transmetalated product, $\mathrm{Pd^{II}}$(NCP2H)–CC–Ph **3**, was also obtained in 19% yield. This unique reductive transmetalation from Ag(III) to Pd(II) inside the NCP core was also observed in the Sonogashira coupling reaction.[9] The reaction of N-confused 3-bromotetrakis[4-(trifluoromethyl)phenyl]porphyrinatocopper(II) complex **4** proceeded in a similar manner to give $\mathrm{Cu^{II}}$(NCP2H)–CC–Ph **5** in 48% yield. Transmetalated product **6** was also isolated in 10% yield. The $\mathrm{AsPh_3}$ ligand so far afforded the better yields than the phosphine ligands such as $\mathrm{PPh_3}$ and diphenylphosphinoethane.

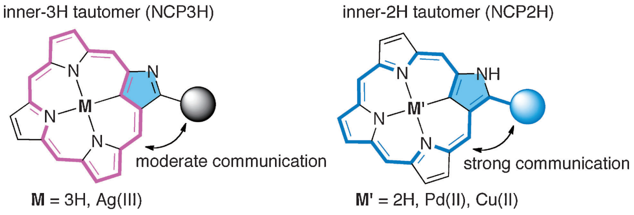
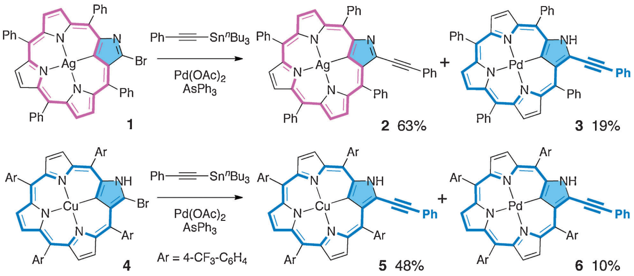
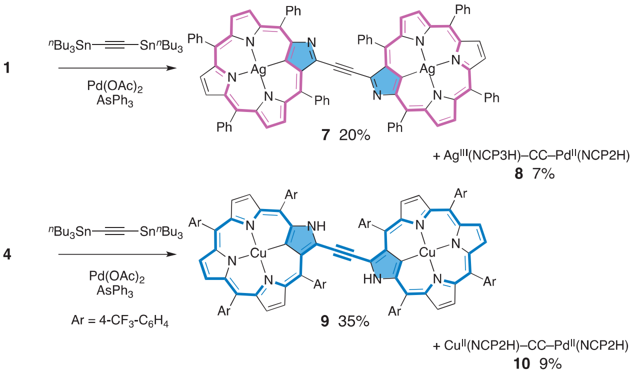


Figure 1. NH-Tautomerization of N-confused porphyrins.



Scheme 1. Synthesis of NCP–CC–Ph.



Scheme 2. Synthesis of NCP dimers.

Then, syntheses of acetylene-bridged NCP dimers were examined by the reactions with bis(tributylstannyl)acetylene (Scheme 2). The Pd-catalyzed reaction of **1** successfully gave $\mathrm{Ag^{III}}$(NCP3H)–CC–$\mathrm{Ag^{III}}$(NCP3H) **7** in 20% yield together with $\mathrm{Ag^{III}}$(NCP3H)–CC–$\mathrm{Pd^{II}}$(NCP2H) **8** in 7% yield. In the ^{1}H NMR spectrum of **7** in $\mathrm{CDCl_3}$, the signals due to β-pyrrolic protons (12H) were observed in the region of δ 8.5–8.9, suggesting its strong aromatic character. Additionally, the number of proton signals indicated the symmetric structure of **7**. Similarly, the reaction of **4** afforded $\mathrm{Cu^{II}}$(NCP2H)–CC–$\mathrm{Cu^{II}}$(NCP2H) **9** in 35% yield and $\mathrm{Cu^{II}}$(NCP2H)–CC–$\mathrm{Pd^{II}}$(NCP2H) **10** in 9% yield. The reactivity of NCP in the Stille coupling would be higher than

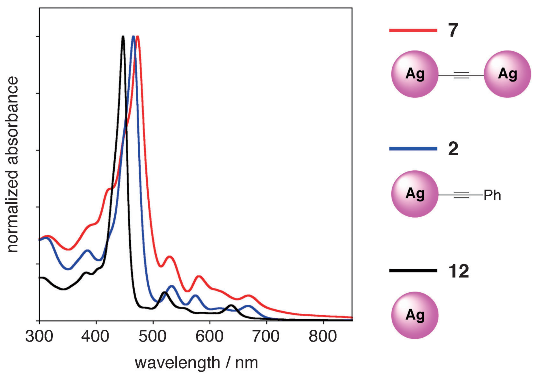


Figure 2. Absorption spectra of **7**, **2**, and **12** in CH_2Cl_2.

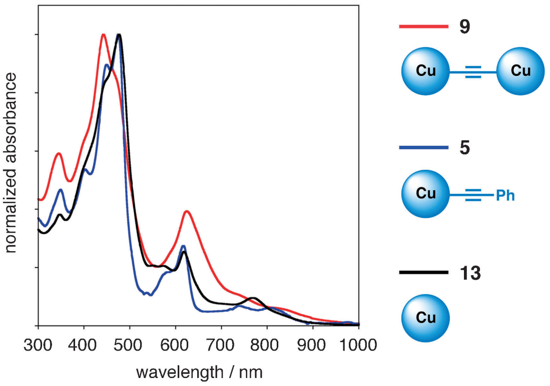
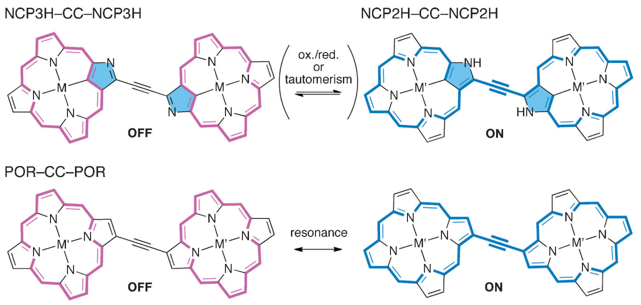


Figure 3. Absorption spectra of **9**, **5**, and **13** in CH_2Cl_2.



Scheme 3. [18]Annulenic π circuit and resonance structures of β,β'-acetylene-bridged regular porphyrin dimer.

Table 1. Properties of acetylene-bridged NCP dimers and regular porphyrin dimer

Compound	State	λ_Q /nm	ε_{Soret} /$M^{-1}\,cm^{-1}$	$FWHM_{Soret}$	OS_{Soret}
7	OFF dimer	667	252000	2486	2.66
12[11]	monomer	637	177000	1329	1
9	ON dimer	830	101000	6810	1.58
13	monomer	768	89100	5694	1.32
11	ON/OFF dimer	609	129000	2562	1.12
14	monomer	585	539000	657	1.28

regular porphyrin: the reaction of β-bromotetraphenylporphyrinatozinc (II) (β-Br–Zn^{II}(TPP)) with bis(tributylstannyl)acetylene gave Zn^{II}(TPP)–CC–Zn^{II}(TPP) (**11**) in 8% yield.[11]

The absorption spectrum of **7** in CH_2Cl_2 was compared with those of **2** and Ag^{III}(NCP3H)[12] (**12**) (Figure 2). In the parent Ag(III) complex **12**, the Soret band was observed at 447 nm and the Q band of the longest wavelength (λ_Q) was observed at 637 nm. Introduction of phenylethynyl group (**2**: 466 and 667 nm) caused a moderate red shifts ($\approx$30 nm) from **12**. The absorption wavelengths of **7** (473 and 667 nm) were similar to those of **2**.

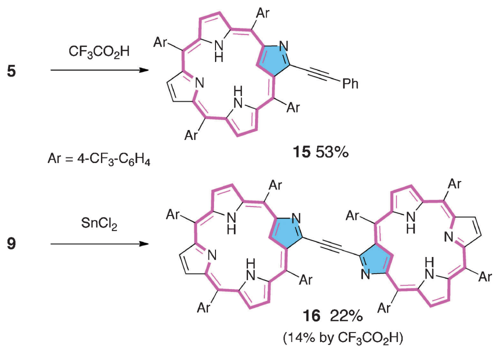
Absorption spectra of **9**, **5**, and Cu^{II}(NCP2H) (**13**) in CH_2Cl_2 are shown in Figure 3. In the parent monomer complex **13**, the Soret band appeared at 477 nm, and λ_Q appeared at 768 nm. In the case of the phenylethynyl derivative **5**, split of the Soret band (449 and 474 nm) as well as the red shift of 43 nm from **13** in λ_Q (811 nm) was observed. Significant broadening and a further red shift of the Q band were observed for **9** ($\approx$830 nm, shoulder).

The uniqueness of 3,3′-acetylene-bridged NCP dimers is made explicit by comparison with β,β'-acetylene-bridged regular porphyrin dimer (POR–CC–POR). In NCP3H–CC–NCP3H, the acetylene moiety and the [18]annulenic π circuit are not connected directly ("OFF" state), while they are connected in NCP2H–CC–NCP2H ("ON" state) although the π circuit is not complete (Scheme 3). Potentially, ON/OFF can be switched by NH-tautomerism or oxidation/reduction.[8,13] In the case of POR–CC–POR, both ON and OFF states can be described depending on the resonance structures. Properties of **7**, **9**, and the corresponding monomer complexes are listed in Table 1. The data of Zn^{II}(TPP)–CC–Zn^{II}(TPP) (**11**) and Zn^{II}(TPP) (**14**) is also shown. Since the energy of λ_Q is a measure of the HOMO–LUMO gap or the porphyrin–porphyrin conjugative interactions in the ground state, the large red shift of **9** from **13** (62 nm) would indicate strong interaction between NCP chromophores at the ON state. Similarly, the moderate red shift of **7** from **12** (30 nm) suggested relatively weak interaction between NCP chromophores at the OFF state. In the case of regular porphyrin **11**, the smaller red shift from **14** (24 nm) was observed, indicating weak porphyrin–porphyrin interaction in the ground state.

The full width at half maximum of the Soret band region ($FWHM_{Soret}$) can be regarded as an approximate measure of the relative extent of porphyrin–porphyrin excitonic coupling in the S_2 state.[11] The $FWHM_{Soret}$ of **7** (2486 cm^{-1}) is similar to that of **11** (2562 cm^{-1}), while the $FWHM_{Soret}$ of **9** (6810 cm^{-1}) is significantly larger than the others. This might be indicative of stronger excitonic coupling in **9** at the ON state. However, the intrinsically large $FWHM_{Soret}$ of NCP monomer complex **13** (5694 cm^{-1}) hampered further discussion.

Thus, the relative oscillator strengths (OS_{Soret})[11,14] of the Soret band region are examined, which would be related to the porphyrin–porphyrin electronic interaction. The OS_{Soret} of **7** (2.66) is much larger than that of **9** (1.58) and **11** (1.12), suggesting weak electronic interaction between NCP chromophores at the OFF state.

Finally, demetalation of the alkynyl-NCP metal complexes was studied (Scheme 4). When **7** was subjected to similar reaction conditions (excess $NaBH_4$) for demetalation of **2** reported previously,[9] progress of the reaction was confirmed by mass analysis (m/z 1250). Unfortunately, isolation of the target free-base compound was so far difficult possibly due to its



Scheme 4. Demetalation of Cu^{II}(NCP2H).

instability. Then, acid-mediated copper demetalation was examined. When **5** was treated with CF_3CO_2H, the corresponding free-base NCP **15** was obtained in 53% yield. Similarly, treatment of **9** with CF_3CO_2H gave the target free-base compound **16** in 14% yield. This time, **16** is stable enough to be isolated with standard silica gel column chromatography because of the electron-withdrawing effect imposed by trifluoromethyl groups. Slight modification of the product yield (22%) was observed in reductive demetalation of **9** by $SnCl_2$.[15] In the ^{1}H NMR spectrum of **16** in $CDCl_3$, the sharp signal due to inner-CH moieties appeared at δ −4.80 (2H), and the broad signal due to inner-NH moieties appeared at δ −2.05 (4H), which indicated successful isolation of the free-base NCP dimer.[16]

In summary, the 3,3′-acetylene-bridged NCP dimers were readily synthesized by one-step three-component Stille coupling reactions. Considerable interactions between the NCP chromophores were suggested by the absorption spectra, in which clear difference was recognized between NCP3H and NCP2H dimers. Strong interaction was suggested for the NCP2H–CC–NCP2H at the ON state and relatively weak interaction was suggested for the NCP3H–CC–NCP3H at the OFF state. Further study including spectroelectrochemistry as well as ESR studies to reveal electronic communication between NCP chromophores in datail will be reported in the near future. Studies on control of NCP2H/NCP3H or ON/OFF state in NCP dimer by external stimuli are also underway.

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