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Syntheses of aryl- and arylethynyl-substituted *N*-confused porphyrins

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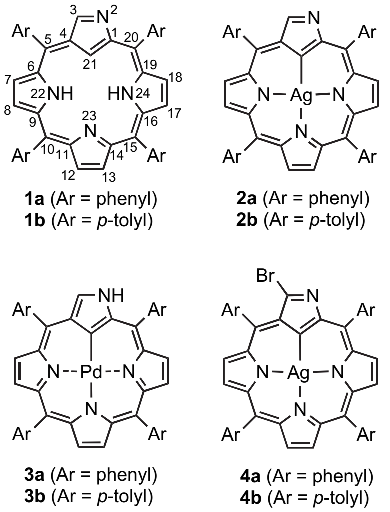
Abstract—Palladium-catalyzed cross-coupling reactions under Suzuki, Sonogashira, and Stille conditions afford 3-aryl (**9**–**12**) and 3-arylethynyl *N*-confused porphyrin (NCP) silver(III) complexes (**13**–**15**) from the 3-bromo NCP complex (**4**) in ca. 70% yields along with the transmetalated products, 3-substituted NCP palladium(II) complexes (**11-Pd** to **15-Pd**), in 10–30% yields. Substitution at 3-position was confirmed by the single crystal X-ray structures of **9**, **13-Ag**, and **13-Pd**. The arylethynyl groups or five-membered heterocyclic aromatic rings at 3-position largely affected the optical properties of *N*-confused porphyrin, in which the longest absorption maxima of the Q-bands are shifted bathochromically by 30–120 nm. The electronic effect of substituent differs largely between palladium and silver complexes reflecting the different π-electron delocalization pathway of NCP cores. 3-Aryl- and 3-arylethynyl NCP silver(III) complexes were easily demetalated to afford the corresponding free base porphyrins by the treatment of sodium borohydride.

1. Introduction

Chemical modification of porphyrin has been attempted vigorously for the model studies of biological functions of porphyrins in photosynthesis, oxygen transport, electron transfer, etc., and for the applications as optical and electronic materials.[1] Whereas a variety of functional groups have been introduced on the porphyrins, the knowledge of the chemical reactivity of porphyrin analogs such as isomeric, expanded, and contracted ones is very limited.[2] Among such analogs, *N*-confused porphyrin (NCP, **1**) and its family have attracted much attention due to the peculiar properties different from the standard porphyrin (Chart 1).[3,4] The unique properties of NCP mainly originate from the confused pyrrole ring connected to the *meso*-carbons through its α- and β′-positions. For example, NCP coordinates various metals in the inner core to stabilize the rare high oxidation states of metals.[5] NCP can utilize the outward-pointing nitrogen of the confused pyrrole for metal coordination to form dimeric and trimeric complexes.[6,7] NCP possesses two different types of stable NH tautomers,[8] and one of the tautomeric forms bearing an outer-NH group exhibits strong anion-binding properties.[5e,l,9] Several functional groups have been introduced on the *meso*-[10] and β-position[11] and on the confused pyrrole ring.[12–14] The confused pyrrole is proved more reactive than other three normal pyrrole rings in the core[12] and in fact the substituents such as bromo,[12a] cyano,[12b] pyrrole,[12c] and hydroxyl groups[12d] have been introduced at the outer $C^{(3)}$-position, and bromo,[12a] chloro,[12a] cyano,[13a] alkyl,[13b] and nitro groups[13c] at the inner $C^{(21)}$-position. The outward-pointing $N^{(2)}$ atom is also selectively alkylated[14a] and the peripheral



1a (Ar = phenyl)
1b (Ar = *p*-tolyl)
2a (Ar = phenyl)
2b (Ar = *p*-tolyl)
3a (Ar = phenyl)
3b (Ar = *p*-tolyl)
4a (Ar = phenyl)
4b (Ar = *p*-tolyl)

Chart 1.

Keywords: *N*-Confused porphyrin; Pd-catalyzed cross-coupling; Ag(III) complex; Pd(II) complex.

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$N^{(2)}$–$C^{(3)}$ bond is shown to serve as a dieneophile for Diels–Alder reaction.[14b] However, there are few reports on the introduction of π-functional groups directly on the NCP framework.[15]

In this context, palladium-catalyzed cross-coupling reactions are of particular interest because they are successfully applied in the syntheses of aryl- and ethynyl-substituted porphyrins for the studies of energy and electron transfer processes.[16,17] Because of the disruption of an 18π-conjugation pathway at the confused pyrrole ring in one of the tautomers, the π-conjugation at the confused pyrrole may largely affect the electronic states and, consequently, the properties of NCP.[8] In this paper, we describe the syntheses of a series of 3-aryl- and 3-arylethynyl NCPs from the novel precursor, 3-bromo NCP silver(III) complex (**4**). Palladium-catalyzed cross-coupling reactions with arylboronic acid, arylacetylene, and aryl(tributyl)stannane have been applied to the complex **4** to yield 3-substituted aryl- and arylethynyl NCPs. Some of them are characterized by single crystal X-ray diffraction analyses.

2. Results and discussion

2.1. Bromination of NCP and synthesis of 3-bromo NCP silver(III) complex (4)

As previously reported,[12a] bromination of NCP with 1 equiv of *N*-bromosuccinimide (NBS) proceeded at the inner $C^{(21)}$-position and, when an excess NBS was used, the second Br attacked at the outer $C^{(3)}$-position, regioselectively (Scheme 1).

The $C^{(21)}$-bromination of NCP was confirmed by the X-ray single crystal structure of the $N^{(2)}$-methyl, $C^{(21)}$-bromo *N*-confused tetraphenylporphyrin (NCTPP) (**8**), where the bromo group is attached at the inner carbon with a C–Br bond length of 1.86(2) Å (Fig. 1). The porphyrin core is largely distorted and the mean deviation from the least-square plane consisting of 24 atoms is 0.40(2) Å. The pyrrole rings of **8** (Pyr1 to Pyr4) are highly tilted against the least-square plane and the dihedral angles of Pyr1 (confused), Pyr2, Pyr3, and Pyr4 are 42.6(5), 24.2(6), 14.3(6), and 22.4(6)°, respectively. Particularly, the tilting of the confused pyrrole ring is larger than that of **1** (24.6(1)°)[3a] and is comparable with that of 21-nitro NCP (41.3(2)°).[12a]

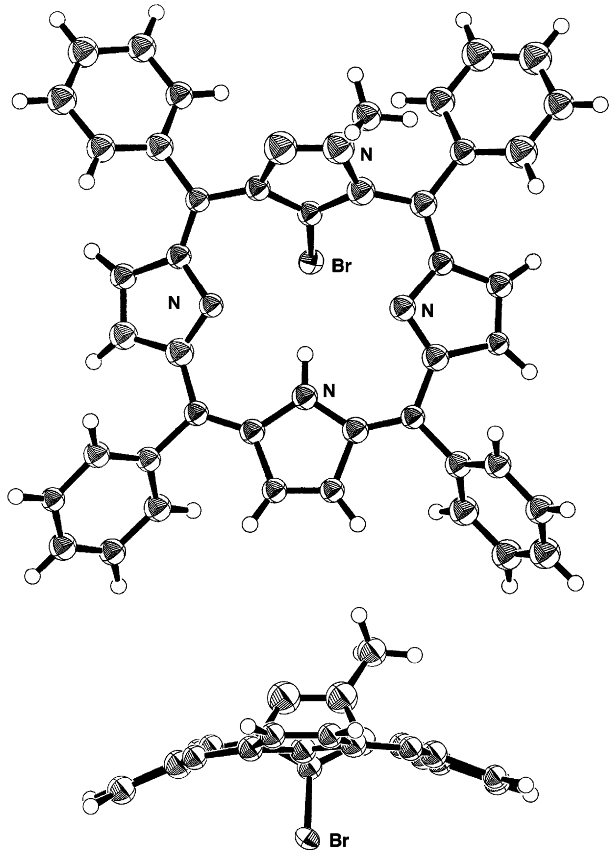
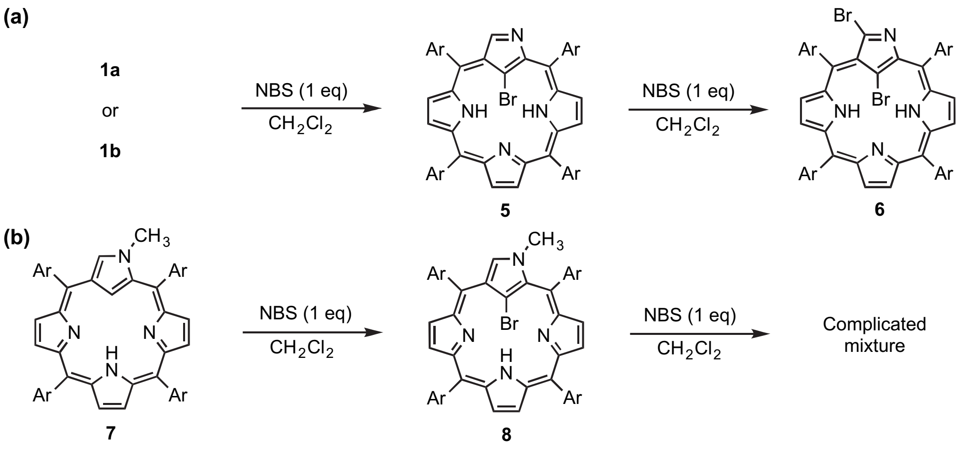


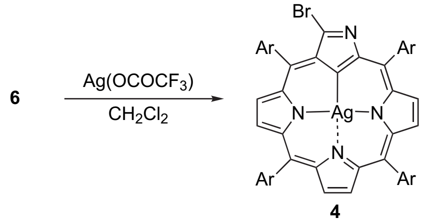
Figure 1. X-ray structure of **8**: (upper) top view and (lower) side view. *meso*-Phenyl groups are omitted for clarity in the side view.

The second bromination of NCP core occurs at the outer $C^{(3)}$-position of the confused pyrrole ring to afford $C^{(3)}$, $C^{(21)}$-dibromo NCP (**6**).[12a] The bromo groups in **5** and **6**, however, were not susceptive for Pd-catalyzed cross-coupling reactions, probably due to the deactivation of Pd catalysts by being captured in the NCP core. Thus, preoccupation of the inner coordination site by Ag atom was attempted.[5a] A treatment of **6** with 4 equiv of silver trifluoroacetate in CH_2Cl_2 afforded the 3-bromo silver(III) complex (**4**), in



Scheme 1.

48% yield (Scheme 2). In this reaction, 1 equiv of Ag(I) ion was consumed to remove the inner bromo group and the other 2 equiv of Ag(I) was used to oxidize the remaining Ag(I) to Ag(III). In the ^{1}H NMR spectrum in $CDCl_3$, the pyrrolic β-proton signals of **4** were observed in the range of 8.6–8.9 ppm, reflecting the diamagnetic nature of the silver(III) complex.

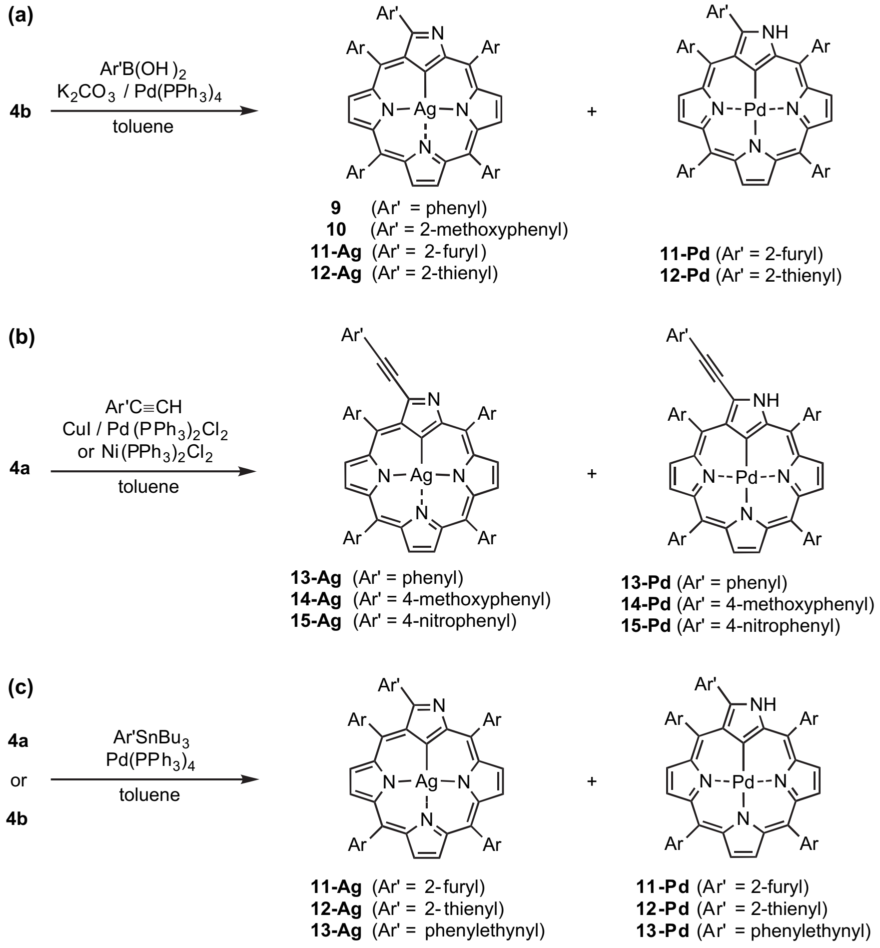


Scheme 2.

2.2. Palladium-catalyzed cross-coupling reactions of NCP

At first, arylation on **4b** was investigated with 10 equiv of phenylboronic acid and potassium carbonate in the presence of catalytic amount of tetrakis(triphenylphosphine)palladium in toluene. After stirring for 3 h at 90 °C under inert atmosphere, the 3-phenyl NCP silver(III) complex (**9**) was obtained in 62% yield (Scheme 3a). In the ^{1}H NMR spectrum of **9** in $CDCl_3$, new signals around 7 ppm along with three pairs of pyrrolic β-hydrogen signals in the range from 8.5 to 9 ppm were observed, which proved the introduction of a phenyl group at the $C^{(3)}$-position in the confused pyrrole ring of **4b**. Other arylboronic acids were also effective for the coupling reactions to afford the corresponding 3-aryl NCPs (Table 1). For example, the reaction of **4b** with 2-methoxyphenylboronic acid afforded 3-(2′-methoxyphenyl) NCP (**10**) in a comparable yield with that of **9**. The reactions with 2-furan- and 2-thiopheneboronic acids, however, afforded the transmetalated product, 3-(2′-furyl) and 3-(2′-thienyl) NCP palladium(II) complexes (**11-Pd** and **12-Pd**) in 13% and 20% yields, respectively. In these reactions, uncharacterized byproducts were obtained along with the starting substrate **4b**. Similar to the NCP palladium(II) complexes (**3**),[6b] the ^{1}H signals of the outer-NH protons for **11-Pd** and **12-Pd** appeared at 10.10 and 9.60 ppm, respectively, and the β-protons resonated in a narrow range of 7.80–7.20 ppm. The signals of the introduced substituents were observed at 6.24 and 5.40 ppm for the furan ring of **11-Pd** and 7.20 and 6.73 ppm for the thiophene ring of **12-Pd**.

When phenylacetylene was subjected to the reaction with **4a** in the presence of catalytic amount of $Pd(PPh_3)_2Cl_2$ and CuI in toluene, the expected coupling product 3-phenylethynyl NCP silver(III) complex (**13-Ag**) was not obtained, but



Scheme 3.

Table 1. The isolated yields of Pd-catalyzed cross-coupling products from **4**

Substrate	Reagent	Product	Yield (%)
4b	Phenylboronic acid	**9**	62
	2-Methoxyphenylboronic acid	**10**	52
	2-Furanboronic acid	**11-Pd**	13 (34)[c]
	2-Thiopheneboronic acid	**12-Pd**	20 (29)[c]
4a	Phenylacetylene[a]	**13-Pd**	14
	4-Methoxyphenylacetylene[a]	**14-Pd**	8
	4-Methoxyphenylacetylene[b]	**14-Ag**	11
	4-Nitrophenylacetylene[a]	**15-Pd**	20
	4-Nitrophenylacetylene[b]	**15-Ag**	15
	Tributyl(2-furylethynyl)tin	**11-Ag**, **11-Pd**	63, 10
	Tributyl(2-thienylethynyl)tin	**12-Ag**, **12-Pd**	68, 7
	Tributyl(phenylethynyl)tin	**13-Ag**, **13-Pd**	76, 10

[a] $Pd(PPh_3)_2Cl_2$.

[b] $Pd(PPh_3)_2Cl_2/Ni(PPh_3)_2Cl_2$.

[c] Recovered **4b**.

similarly to the reactions with 2-furan- and 2-thiopheneboronic acids, the transmetalated one, 3-phenylethynyl NCP palladium(II) complex (**13-Pd**), was formed in 14% yield (Scheme 3b). The signals of the outer-NH and the phenylethynyl moiety were observed at 9.92 and 7.28–7.20 ppm in the ^1H NMR spectrum of **13-Pd** in $CDCl_3$. When the catalyst for the Sonogashira coupling was changed from $Pd(PPh_3)_2Cl_2$ into a mixture of $Pd(PPh_3)_2Cl_2/Ni(PPh_3)_2Cl_2$, the transmetalation was hampered and 3-(4′-nitrophenylethynyl) NCP silver(III) complex (**14-Ag**) and 3-(4′-methoxyphenylethynyl) silver(III) complex (**15-Ag**) were obtained in moderate yields (11–15%).

By using the Stille conditions with corresponding tributyltin reagents, the 3-furyl-, 3-thienyl-, and 3-phenylethynyl NCP silver(III) complexes (**11-Ag** to **13-Ag**) were obtained in high yields (63–76%) (Scheme 3c). Simultaneously, transmetalated products were isolated in ca. 10% yields. Similar to other silver(III) complexes (**3**, **4**, **9**, and **10**), the ^1H NMR spectra of **11-Ag** to **13-Ag** in $CDCl_3$ showed the complicated β-proton signals in the range of 8.90–8.50 ppm probably due to the coupling with the central silver atom.

The reaction mechanism of the transmetalation by the Pd catalysts has not been clearly revealed yet, but it may relate to the stability of the NCP silver(III) complexes. The coordinated silver atom in the NCP ligand is easily demetalated under the reductive conditions in the coupling reaction (vide infra). Thus, when relatively mild reagents such as phenylacetylene are used, the competitive demetalation reaction may be involved during the coupling reaction. As a result, 3-bromo NCP palladium(II) complex (**16**) could be formed by the reaction of uncoordinated NCP ligand and Pd catalysts (Fig. 2). The reactivities of the two 3-bromo NCP complexes, silver(III) (**4**) and palladium(II) (**16**), might be different and probably the latter is more reactive, because the reactions with furan- and thiopheneboronic acid and arylacetylene afforded only palladium complexes with the recovery of starting materials (**4**). On the other hand, when the more reactive tributylstannyl reagents were used, the yields of the coupling silver(III) complex were increased largely, probably indicating that the coupling reaction proceeded faster than the demetalation of **4**.

2.3. X-ray structures

The $C^{(3)}$-arylation of **4** has been confirmed by the single crystal analysis of **9** (Fig. 3a). In the crystal, the molecule is slightly distorted from the least-square plane consisting of core 24 atoms with the mean deviation of 0.20(2) Å, reflecting a small ionic size of silver(III). The Ag atom locates 0.038(7) Å above the core CNNN plane and the bond distances of Ag–C and three Ag–N bonds are 2.00(1) and 2.04(1), 2.08(1), and 2.060(9) Å, respectively, which are comparable with the bond lengths of Ag–C (1.99–2.03 Å) and Ag–N (2.04–2.07 Å) of **2a**[5a] and doubly *N*-confused porphyrin silver(III) complexes.[5b] The introduced phenyl group (ϕ_5) at the 3-position is almost parallel (160.9(6)°) to the neighboring *meso*-tolyl group (ϕ_1) forming a π-stacking pair with a distance of 2.84(3) Å.

The X-ray structure of **13-Ag** displays the similar distortion as that of **9**, and the mean deviation of the porphyrin plane is 0.15(2) Å (Fig. 3b). The introduced phenylethynyl group is arranged parallel to the NCP plane and the dihedral angle between the benzene ring (ϕ_5) and the NCP plane is 3.5(7)°. The bond lengths of Ag–C and three Ag–N bonds are 2.021(6), 2.05(1), 2.048(6), and 2.05(1) Å, respectively.

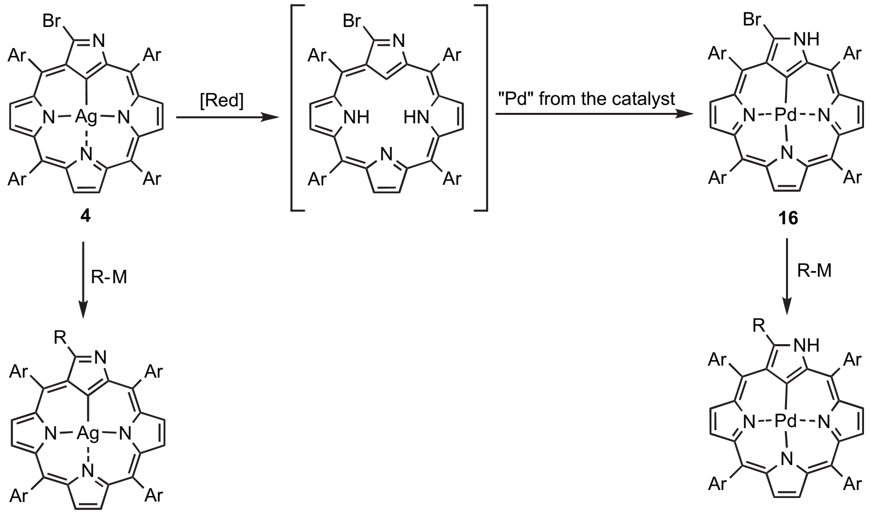


Figure 2. A plausible reaction mechanism of the transmetalation of **4**.

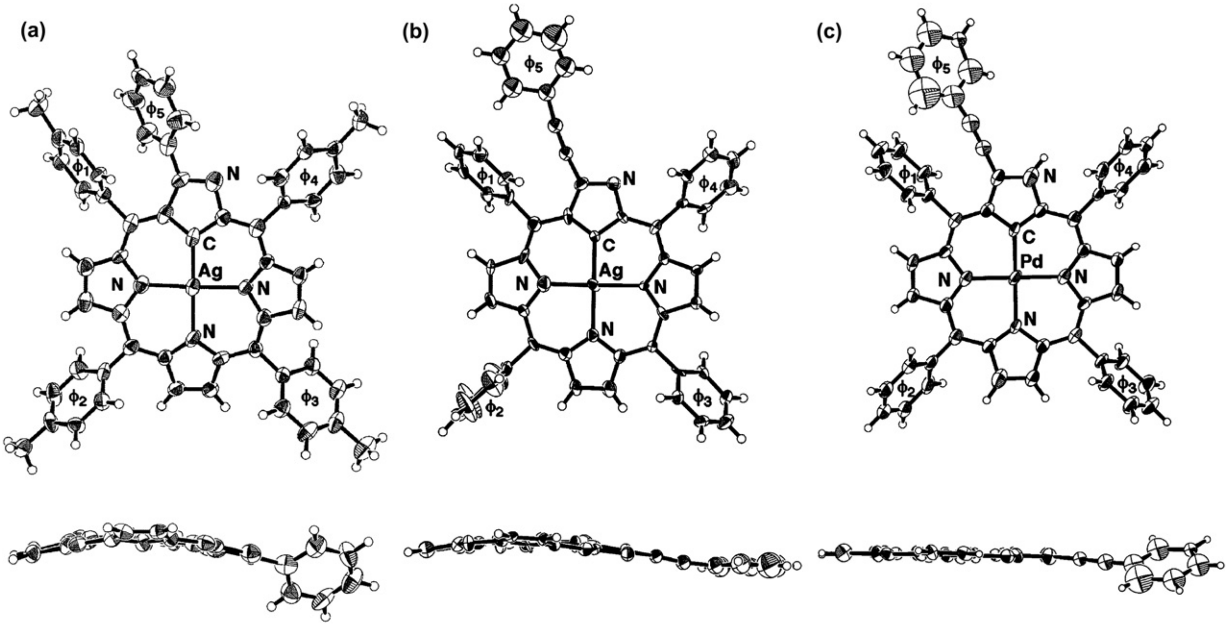


Figure 3. X-ray structures of (a) **9**, (b) **13-Ag**, and (c) **13-Pd**. *meso*-Aryl groups are omitted for clarity in side views.

In the X-ray structure of **13-Pd**, the molecule is rather planar with the mean deviation of the core plane being only 0.02(1) Å and the palladium atom is located in the middle of CNNN plane (Fig. 3c). The highly planar structure of **13-Pd** is also reflected from the size-matching of the NCP ligand and palladium atom, showing the bond distances of Pd–C and three Pd–N bonds to be 2.029(9), 2.030(9), 2.03(1), and 2.034(8) Å, respectively.[6b] Introduced phenyl ring (ϕ$_5$) and the NCP core plane are nearly parallel with a dihedral angle of 5.8(8)°.

2.4. Optical absorption spectra of NCP derivatives

The absorption spectra of $C^{(3)}$-substituted NCP silver(III) complexes in CH_2Cl_2 are almost same as that of **2a**[5a] and **4** (Fig. 4, Table 2). On the other hand, the corresponding palladium(II) complexes exhibit the electronic communication between the $C^{(3)}$-substituents and the NCP core. Particularly, three 3-arylethynyl NCPs (**13-Pd** to **15-Pd**) display significant substituent effect and the longest Q-bands show the bathochromic shifts (~40 nm) by the introduction of electron-donating substituents at the *para*-position of the arylethynyl groups. The large change of the absorption profiles of **11-Pd** to **15-Pd** could be attributed to the delocalization of π-electrons of the NCP core over the aryl- and arylethynyl groups.

The marked difference of the substituent effect on the absorption spectra between the silver(III) and palladium(II) complexes could be ascribable to the difference of the electronic delocalization pathway of the NCP cores in the complexes (Fig. 5). In the silver complexes, the aromatic circuits can be drawn by avoiding the $C^{(3)}$–$N^{(2)}$ imino-bond. Then, the electronic effect of the substituents through the $C^{(3)}$-position should be less pronounced because the substituents are not directly connected to the π-conjugation of the NCP

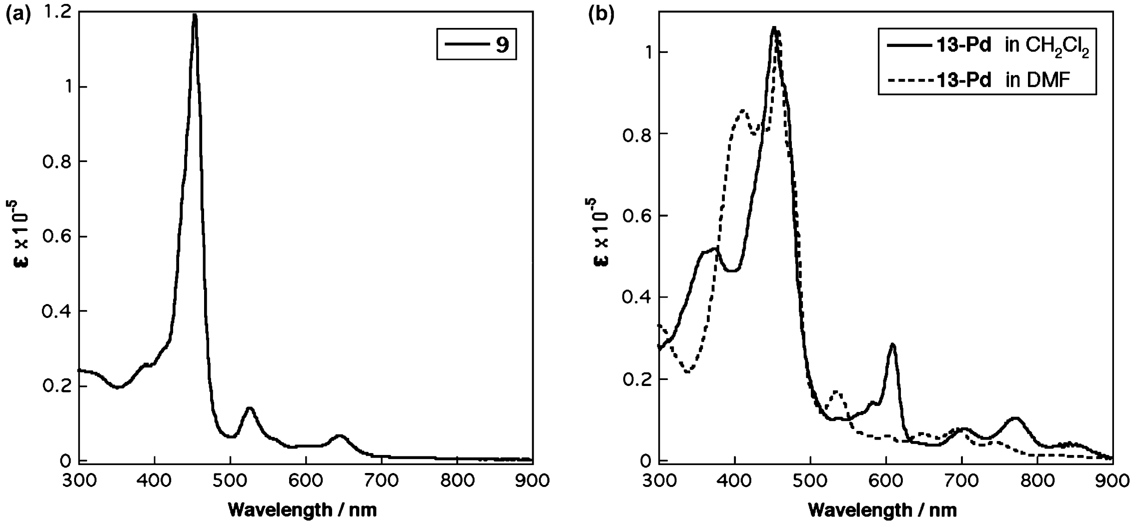


Figure 4. Optical absorption spectra of (a) **9** in CH_2Cl_2 and (b) **13-Pd** in CH_2Cl_2 and DMF.

Table 2. Optical absorption maxima of **1–4** and **9–15** in CH_2Cl_2

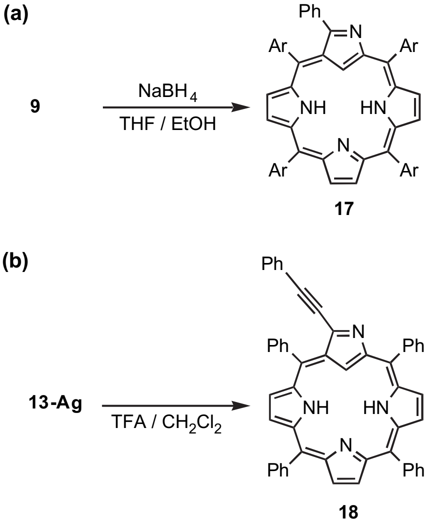
Compound	N-band	Soret	Q_{I}	Q_{II}	Q_{III}	Q_{IV}	Q_{V}
1a[a]	—	438	539	582	—	730	—
2a[b]	—	447	520	—	637	—	—
3b[c]	377	447	534	577	643	700	766
4a	—	450	522	590	639	—	—
9	—	454	527	—	646	—	—
10	—	452	524	—	641	—	—
11-Ag	—	457	528	608	657	—	—
11-Pd	374	466	558	606	676	735	810
12-Ag	—	457	530	—	654	—	—
12-Pd	381	458	545	591	663	718	791
13-Ag	384	464	532	574	615	666	—
13-Pd	357	468	567	609	695	762	842
14-Ag	383	467	533	576	614	666	—
14-Pd	354	473	577	619	719	791	883
15-Ag	398	467	533	577	617	666	—
15-Pd	362	472	569	612	686	752	832

[a] Ref. 3a.
[b] Ref. 5a.
[c] Ref. 6b.

core. On the other hand, the aromaticity of the Pd(II) complexes, in which the delocalization pathway is disrupted at the confused pyrrole, is attributed to the zwitterionic resonance forms shown in Figure 5. Then, the $C^{(3)}$-substituents are directly linked to the conjugation pathway, which causes the electronic perturbation of the NCP core. The absorption spectra of palladium complexes also show a large solvent effect, which was not observed in the silver(III) complexes. For example, the spectrum of **13-Pd** in dimethylformamide (DMF) exhibited the hypsochromic shifts of the Q-bands and characteristic N-band beside the Soret band, compared to that in CH_2Cl_2 (Fig. 4b). The hydrogen bond between the outer-NH of the confused pyrrole and the solvent molecules may stabilize the zwitterionic resonance forms in **13-Pd**. Supporting this, the absorption spectra of **3a** also displayed similar solvent effect, and thus, the outer-NH of **13-Pd** may serve as the inlet of the external stimuli to the NCP core.[5e]

2.5. Demetalation of NCP derivatives

The silver atom of **9** was easily demetalated to afford 3-phenyl NCP free base (**17**) in 70% yield by a treatment with $NaBH_4$ (Scheme 4).[18] The ^1H NMR signal of the inner $C^{(21)}$–H was observed at −4.56 ppm, which is slightly lower-field shifted compared to that of **1** (−5.1 ppm) in $CDCl_3$.[3a] The silver atom of **13-Ag** was also easily demetalated by trifluoroacetic acid (TFA) as well as $NaBH_4$ to afford the free base, 3-phenylethynyl NCP (**18**), which displayed the ^1H NMR signal of the inner $C^{(21)}$–H at −4.70 ppm in $CDCl_3$. The absorption spectra of **17** and **18** are shown in Figure 6, where the Soret bands are ca. 15–30 nm bathochromic shifted compared to unsubstituted NCTPP (**1a**).



Scheme 4.

3. Summary and conclusions

Palladium-catalyzed cross-coupling reactions of *N*-confused porphyrin (NCP) silver(III) complex with arylboronic acid, arylacetylene, and aryl(tributyl)tin were examined for the first time. Arylation and ethynylation at the confused pyrrole ring cause remarkable π-conjugation effects that are not observed in the normal tetraarylporphyrin. The transmetalation of the central silver atom to palladium atom was observed in the coupling reactions. In addition, the demetalation procedure of the silver(III) NCP complex was developed. The aromatic and π-conjugated substituents at 3-position largely

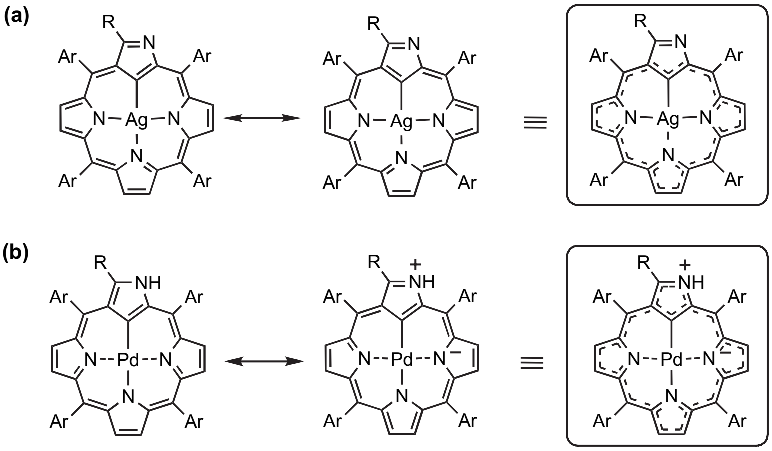


Figure 5. Conjugation pathways in (a) NCP silver(III) and (b) NCP palladium(II) complexes.

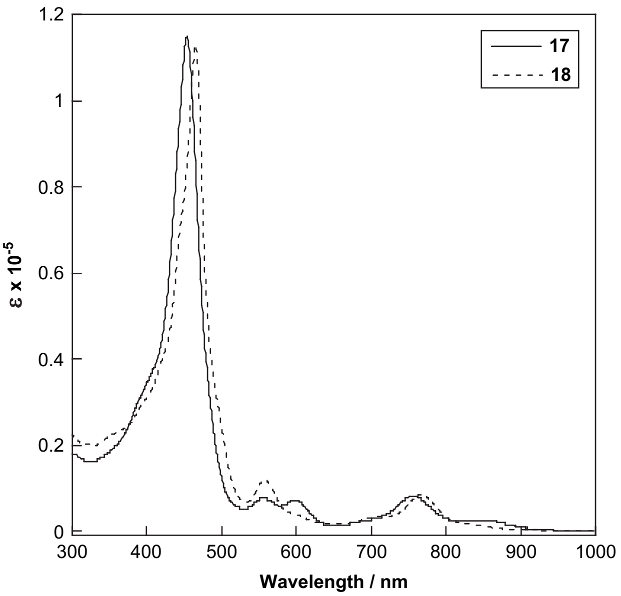


Figure 6. Optical absorption spectra of **17** and **18** in CH_2Cl_2.

affected the optical properties of *N*-confused porphyrin, especially in the palladium(II) complexes, reflecting the different π-electron delocalization pathway of NCP cores. As the Pd-catalyzed coupling reactions could afford a variety of NCP derivatives, the design and synthesis of a variety of functional molecules based on NCP would become more facile.

4. Experimental

4.1. General

Commercially available reagents and solvents were used without further purification unless otherwise mentioned. NCP (**1a**: NCTPP, Ar=phenyl; **1b**: NCTTP, Ar=*p*-tolyl) and the dibromo derivatives (**6a**, **6b**) were synthesized by the reported procedures.[3,12a] Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554). UV/visible spectra were recorded on a Shimadzu UV-3100PC spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL α-500 spectrometer (operating at 500.00 MHz for ^1H and 125.65 MHz for ^{13}C), JEOL JNM-AI270 (operating at 300.40 MHz for ^1H) and JEOL ECP-400 (operating at 100.53 MHz for ^{13}C) using deuterated chloroform or deuterated dichloromethane as the internal lock and the residual solvent as the internal reference. Fast atom bombardment mass spectra (FABMS) were recorded on a JEOL-HX110 in the positive ion mode with a xenon primary atom beam with 3-nitrobenzyl alcohol as matrix. MALDI-TOF mass spectra were recorded on a Voyager-DE RP in the positive ion mode with dithranol matrix.

4.1.1. 3-Br NCTPP silver(III) complex (4a). Silver trifluoroacetate (256 mg, 1 mmol) was added to the solution of 3,21-dibromo NCTPP (**6a**) (200 mg, 0.259 mmol) in dichloromethane (200 mL), and stirred for 1 h at room temperature. After washing by water, the solvent was dried over anhydrous sodium sulfate and removed under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent and the green fraction was collected. The solvent was evaporated and the residue was recrystallized from CH_2Cl_2–hexane, resulting in a dark-purple crystal of **4a** (99 mg) in 48% yield. ^1H NMR ($CDCl_3$): δ (ppm) 8.85 (dd, *J*=5.1, 1.5 Hz, 1H), 8.59–8.67 (m, 5H), 8.18 (dd, *J*=7.8, 1.6 Hz, 2H), 8.08–8.14 (m, 4H), 7.95–7.98 (m, 2H), 7.71–7.77 (m, 12H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 639 (3.87), 522 (4.13), 450 (5.13). HRMS: calcd for $C_{44}H_{27}N_4AgBr$ [M^++1], 798.4764; found 798.4888.

4.1.2. 3-Br NCTTP silver(III) complex (4b). The procedure was same as that of **4a**. 3,21-Dibromo NCTTP (**6b**) (92.1 mg, 0.111 mmol), silver trifluoroacetate (100.6 mg, 0.455 mmol), and dichloromethane (80 mL) as solvent were used. Recrystallization from CH_2Cl_2–hexane afforded a dark-purple crystal of **4b** (45.9 mg) in 48% yield. ^1H NMR ($CDCl_3$): δ (ppm) 8.83 (d, *J*=5.0 Hz, 1H), 8.61 (m, 5H), 8.07 (d, *J*=8.0 Hz, 2H), 7.97 (t, *J*=8.0 Hz, 4H), 7.82 (d, *J*=7.5 Hz, 2H), 7.52 (m, 8H), 2.69 (s, 3H), 2.68 (s, 3H), 2.67 (s, 3H), 2.65 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 641 (3.87), 524 (4.13), 452 (5.13). HRMS: calcd for $C_{48}H_{35}N_4AgBr$ [M^++1], 853.1096; found 853.1104.

4.1.3. $N^{(2)}$-Methyl, 21-bromo NCTPP (8). The synthetic procedure of $N^{(2)}$-methyl NCTPP (**7**) followed the previous report.[14a] To the solution of **7** (30.96 mg, 0.0491 mmol) in CH_2Cl_2 (60 mL) was added 1 equiv of NBS (9.11 mg, 0.0512 mmol) and the mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel eluted with 5% methanol–CH_2Cl_2. The second fraction containing **8** was collected and evaporated. The residue was recrystallized from CH_2Cl_2–methanol to afford a green crystal of **8** (13.72 mg) in 38% yield. The ^1H NMR spectrum of **8** shows very broad signals. ^1H NMR ($CDCl_3$): δ (ppm) 8.20 (m, 4H), 7.82 (m, 23H), 5.91 (br s, 1H), 3.25 (br s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] 827, 710, 646, 575, 457. FABMS: *m*/*z*=707.25 [M^++1]. Calcd for 707.18.

4.1.4. 3-Ph NCTTP silver(III) complex (9). To a 50 mL round bottom flask, **4b** (15.87 mg, 18.57 μmol), phenylboronic acid (22.73 mg, 0.187 mmol), potassium carbonate (71.53 mg, 0.518 mmol), and tetrakis(triphenylphosphine)-palladium (14.5 mg, 12.5 μmol) were added under inert atmosphere. Distilled toluene (5 mL) was added to the flask and then the mixture was degassed by repeated freeze–pump–thaw cycles and stirred for 5 h at 80 °C under Ar. The reaction mixture was washed by water and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel eluted with 3% methanol–CH_2Cl_2. The second green fraction was collected and the solvent was evaporated. The residue was recrystallized from CH_2Cl_2–hexane to afford a dark-purple crystal of **9** (9.85 mg) in 62% yield. ^1H NMR ($CDCl_3$): δ (ppm) 8.88 (dd, *J*=4.8, 1.2 Hz, 1H), 8.79 (dd, *J*=5.2, 1.6 Hz, 1H), 8.63 (m, 4H), 8.17 (d, *J*=8.0 Hz, 2H), 8.03 (d, *J*=8.0 Hz, 2H), 8.00 (d, *J*=8.0 Hz, 2H), 7.67 (d, *J*=8.0 Hz, 2H), 7.53 (m, 8H), 7.13 (m, 3H), 7.01 (d, *J*=7.6 Hz, 2H), 2.70 (s, 3H), 2.69 (s, 3H), 2.61 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$): δ (ppm) 146.60, 141.90, 140.91, 140.25, 139.85 (d, *J*=38.3 Hz), 139.45, 138.42, 138.38, 138.34, 138.01, 137.76, 137.73, 137.24, 136.39, 135.86, 135.52, 135.15, 133.82, 132.78, 132.13, 132.04, 131.48, 130.80, 130.76, 130.26, 129.83, 129.79, 129.52, 128.71, 128.55, 128.42, 127.94, 127.82, 127.80, 127.75, 127.42, 121.38 (d, J=1.5 Hz), 120.11 (d, J=1.5 Hz), 118.21, 21.52. UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 646 (3.82), 527 (4.12), 454 (5.08). HRMS: calcd for $C_{54}H_{39}N_4Ag$ [M^++1], 851.2304; found 851.2303.

4.1.5. 3-(2′-Methoxyphenyl) NCTTP silver(III) complex (10). The procedure was almost same as that of **9**. **4b** (11.56 mg, 0.0135 mmol), 2-methoxyphenylboronic acid (20.68 mg, 0.136 mmol), potassium carbonate (19.85 mg, 0.143 mmol), and tetrakis(triphenylphosphine)palladium (3.56 mg, 3.08 μmol) and distilled toluene (2 mL) as solvent were used. The reaction mixture was stirred for 16 h at 90 °C under Ar. Recrystallization from CH_2Cl_2–hexane afforded a dark-purple crystal of **10** (6.24 mg) in 52% yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (dd, J=5.1, 1.8 Hz, 1H), 8.67 (m, 3H), 8.59 (d, J=4.8 Hz, 2H), 8.16 (d, J=7.2 Hz, 2H), 8.01 (m, 4H), 7.73 (m, 8H), 7.18 (m, 2H), 6.98 (m, 3H), 6.76 (d, J=7.2 Hz, 1H), 6.36 (d, J=8.1 Hz, 1H), 3.66 (s, 3H), 2.69 (s, 3H), 2.68 (s, 3H), 2.59 (s, 3H), 2.38 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 641 (3.78), 524 (4.09), 452 (5.06). HRMS: calcd for $C_{55}H_{41}N_4AgO$ [M^++1], 881.2410; found 881.2390.

4.1.6. 3-(2′-Furyl) NCTTP silver(III) complex (11-Ag). To a 50 mL round bottom flask, **4b** (10.48 mg, 0.0123 mmol) and tetrakis(triphenylphosphine)palladium (2.37 mg, 2.05 μmol) were added under inert atmosphere. Distilled toluene (2 mL) and 2-(tributylstannyl)furan (40 μL) were added to the flask, degassed by repeated freeze–pump–thaw cycles, and stirred for 15 h at 90 °C under Ar. The reaction mixture was washed by water and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel eluted with 3% methanol–CH_2Cl_2. The first fraction contained **11-Pd** and the second green fraction included **11-Ag**. The solvent was evaporated and each residue was recrystallized from CH_2Cl_2–hexane to afford dark-purple crystals of **11-Pd** (1.0 mg) and **11-Ag** (6.5 mg), in 10% and 63% yields, respectively. ^{1}H NMR ($CDCl_3$) for **11-Ag**: δ (ppm) 8.86 (dd, J=4.8, 1.5 Hz, 1H), 8.77 (dd, J=4.8, 1.5 Hz, 1H), 8.60 (m, 4H), 8.15 (d, J=7.8 Hz, 2H), 7.99 (m, 4H), 7.87 (d, J=7.5 Hz, 2H), 7.54 (d, J=7.2 Hz, 8H), 7.02 (br s, 1H), 6.73 (d, J=3.3 Hz, 1H), 6.28 (dd, J=3.3, 1.5 Hz, 1H), 2.69 (s, 3H), 2.68 (s, 3H), 2.63 (s, 3H), 2.53 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 657 (3.77), 528 (4.11), 457 (5.00). HRMS: calcd for $C_{52}H_{37}N_4AgO$ [M^+], 840.2018; found 840.1985.

4.1.7. 3-(2′-Furyl) NCTTP palladium(II) complex (11-Pd). The procedure was almost same as that of **9**. **4b** (10.32 mg, 0.0121 mmol), 2-furanboronic acid (14.32 mg, 0.128 mmol), potassium carbonate (17.54 mg, 0.126 mmol), and tetrakis(triphenylphosphine)palladium (2.65 mg, 2.29 μmol) and distilled toluene (2 mL) as solvent were used. The reaction mixture was stirred for 14 h at 90 °C under Ar. After removal of the solvent, the residue was chromatographed on silica gel eluted with CH_2Cl_2 and the second and the third green fractions were evaporated. Then each residue was recrystallized from CH_2Cl_2–hexane to afford dark-purple crystals of **11-Pd** (1.33 mg) and **4b** (3.53 mg) in 13% and 34% yields, respectively. ^{1}H NMR ($CDCl_3$): δ (ppm) 10.10 (s, 1H), 7.80 (m, 14H), 7.40 (m, 8H), 6.24 (m, 1H), 5.40 (d, J=3.9 Hz, 2H), 2.62 (s, 3H), 2.58 (s, 6H), 2.53 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 810 (3.93), 735 (3.98), 676 (3.90), 606 (4.46), 558 (4.09), 466 (4.97), 374 (4.70). HRMS: calcd for $C_{52}H_{37}N_4PdO$ [M^+], 840.2080; found 840.2022.

4.1.8. 3-(2′-Thienyl) NCTTP silver(III) complex (12-Ag). The procedure was same as that of **11-Ag**. **4b** (12.52 mg, 0.0147 mmol), 2-(tributylstannyl)thiophene (50 μL), tetrakis(triphenylphosphine)palladium (2.43 mg, 2.10 μmol), and distilled toluene (2 mL) as solvent were used. The reaction mixture was stirred for 15 h at 90 °C under Ar. The first fraction contained **12-Pd** and the second green fraction included **12-Ag**. The solvent was evaporated and each residue was recrystallized from CH_2Cl_2–hexane to afford dark-purple crystals of **12-Pd** (0.9 mg) and **12-Ag** (8.5 mg) in 7% and 68% yields, respectively. ^{1}H NMR ($CDCl_3$) for **12-Ag**: δ (ppm) 8.88 (dd, J=4.8, 1.5 Hz, 1H), 8.78 (dd, J=4.8, 1.5 Hz, 1H), 8.60 (m, 4H), 8.17 (d, J=8.1 Hz, 2H), 8.00 (m, 4H), 7.84 (d, J=7.8 Hz, 2H), 7.54 (d, J=7.5 Hz, 8H), 7.18 (br s, 1H), 6.65 (m, 2H), 2.69 (s, 3H), 2.68 (s, 3H), 2.63 (s, 3H), 2.51 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 654 (3.85), 530 (4.20), 457 (5.06). HRMS: calcd for $C_{52}H_{37}N_4AgS$ [M^+], 856.1790; found 856.1885.

4.1.9. 3-(2′-Thienyl) NCTTP palladium(II) complex (12-Pd). The procedure was almost same as that of **9**. **4b** (27.13 mg, 0.0317 mmol), 2-thiopheneboronic acid (41.94 mg, 0.328 mmol), potassium carbonate (47.06 mg, 0.339 mmol), and tetrakis(triphenylphosphine)palladium (8.25 mg, 7.14 μmol) and distilled toluene (2 mL) as solvent were used. The reaction mixture was stirred for 24 h at 90 °C under Ar. After removal of the solvent, the residue was chromatographed on silica gel eluted with CH_2Cl_2 and the second and the third green fractions were evaporated. Then each residue was recrystallized from CH_2Cl_2–hexane to afford dark-purple crystals of **12-Pd** (5.49 mg) and **4b** (7.8 mg) in 20% and 29% yields, respectively. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.60 (s, 1H), 7.83 (m, 8H), 7.55 (m, 2H), 7.45 (d, J=7.8 Hz, 2H), 7.39 (m, 4H), 7.20 (m, 2H), 7.00 (m, 4H), 6.73 (m, 2H), 2.57 (s, 9H), 2.38 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 791 (3.99), 718 (3.96), 663 (3.69), 591 (4.25), 545 (4.05), 458 (5.05), 381 (4.70). HRMS: calcd for $C_{52}H_{37}N_4PdS$ [M^+], 856.1852; found 856.1762.

4.1.10. 3-Phenylethynyl NCTPP silver(III) complex (13-Ag). The procedure was same as that of **11-Ag**. **4a** (50.0 mg, 0.062 mmol), tributyl(phenylethynyl)stannane (30 μL), tetrakis(triphenylphosphine)palladium (8.0 mg, 6.9 μmol), and distilled toluene (15 mL) as solvent were used. The reaction mixture was stirred for 2 h at 90 °C under Ar. The solvent was evaporated and the residue was chromatographed on silica gel eluted with CH_2Cl_2–hexane (2:3). The first fraction contained **13-Pd** and the second green fraction included **13-Ag**. After removal of the solvents, each residue was recrystallized from CH_2Cl_2–hexane to afford dark-purple crystals of **13-Pd** (4.9 mg) and **13-Ag** (37 mg) in 10% and 76% yields, respectively. ^{1}H NMR ($CDCl_3$) for **13-Ag**: δ (ppm) 8.81 (dd, J=4.8, 1.7 Hz, 1H), 8.60–8.54 (m, 5H), 8.22 (dd, J=8.0, 1.7 Hz, 2H), 8.12–8.07 (m, 6H), 7.77–7.58 (m, 13H), 7.40–7.30 (m, 4H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 666 (3.76), 574 (4.02), 532 (4.17), 464 (4.97), 384 (4.44). UV/vis (DMF): λ_{max} [nm] 784, 715, 656, 588.5, 545.5, 485.5, 395. HRMS: calcd for $C_{52}H_{32}N_4Ag$ [M^++1] 819.1678; found 819.1736.

4.1.11. 3-Phenylethynyl NCTPP palladium(II) (13-Pd). A mixture of **4a** (31.02 mg, 0.039 mmol), phenylacetylene (0.02 mL, 0.018 mmol), and triethylamine (10 mL, 71.88 mmol) in distilled toluene (9 mL) was stirred and degassed with Ar and then dichloro-bis(triphenylphosphine)-palladium (5.0 mg, 0.007 mmol) and copper iodide (7.7 mg, 0.041 mmol) were added. The reaction mixture was then stirred for 10 h at room temperature. The solvent was evaporated under vacuum and the residue was chromatographed on silica gel eluted with CH_2Cl_2–hexane (1:1). The first green fraction was evaporated and the residue was recrystallized from CH_2Cl_2–methanol to afford a dark-purple crystal of **13-Pd** (4.3 mg) in 14% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 9.92 (s, 1H), 7.75–7.88 (m, 10H), 7.51–7.66 (m, 15H), 7.20–7.28 (m, 5H). ^{13}C NMR (CD_2Cl_2): δ 81.96, 105.57, 119.00, 119.96, 121.62, 137.41, 137.93, 140.20, 141.82, 141.92, 143.06, 144.81, 147.70, 149.38, 150.17, 152.02. UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 842 (3.67), 762 (4.03), 695 (3.95), 609 (4.45), 567 (4.18), 468 (5.03), 357 (4.74). UV/vis (DMF): λ_{max} [nm] (log ε) 744 (3.63), 694 (3.88), 648 (3.80), 603 (3.76), 535 (4.23), 458 (5.02), 435 (4.92), 412 (4.94). HRMS: calcd for $C_{52}H_{32}N_4Pd$ [M^++1], 819.1740; found 819.1705.

4.1.12. 3-(4′-Methoxyphenylethynyl) NCTPP silver(III) complex (14-Ag). The procedure was same as that of **13-Pd**. **4a** (50.0 mg, 0.062 mmol), 4-methoxyphenylacetylene (50 μL), dichloro-bis(triphenylphosphine)palladium (5.0 mg, 7.1 μmol), dichloro-bis(triphenylphosphine)nickel (5.0 mg, 7.6 μmol), copper iodide (3.0 mg, 16 μmol), triethylamine (66 μL), and distilled toluene (25 mL) as solvent were used. The reaction mixture was stirred for 2 h at 90 °C under Ar. After removal of the solvent, the residue was recrystallized from CH_2Cl_2–methanol to afford a violet crystal of **14-Ag** (6.0 mg) in 11% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.81 (dd, J=5.0, 1.7 Hz, 1H), 8.67–8.54 (m, 5H), 8.23 (d, J=7.2 Hz, 2H), 8.14–8.07 (m, 6H), 7.75–7.62 (m, 12H), 7.31 (d, J=8.7 Hz, 2H), 6.84 (d, J=8.7 Hz, 2H), 3.86 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 666 (3.65), 614 (3.65), 576 (3.93), 533 (3.98), 467 (4.83), 383 (4.30). HRMS: calcd for $C_{53}H_{33}N_4AgO$ [M^++1], 849.1784; found 849.1826.

4.1.13. 3-(4′-Methoxyphenylethynyl) NCTPP palladium(II) complex (14-Pd). The procedure was almost same as that of **13-Pd**. **4a** (15.96 mg, 20 μmol), 4-methoxyphenylacetylene (2.64 mL), dichloro-bis(triphenylphosphine)palladium (2.51 mg, 4 μmol), copper iodide (3.86 mg, 20 μmol), triethylamine (3 mL), and distilled toluene (5 mL) as solvent were used. The reaction mixture was stirred for 18 h at room temperature under argon atmosphere. Recrystallization from CH_2Cl_2–methanol afforded a dark-purple crystal of **14-Pd** (1.4 mg) in 8% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 9.77 (s, 1H), 7.18–7.94 (m, 27H), 6.84 (d, J=8.1 Hz, 2H), 3.85 (s, 3H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 832 (3.60), 752 (3.68), 686 (3.56), 612 (4.52), 569 (4.00), 472 (4.82), 362 (4.50). HRMS: calcd for $C_{53}H_{33}N_4PdO$ [M^+], 848.1767; found 848.1749.

4.1.14. 3-(4′-Nitrophenylethynyl) NCTPP silver(III) complex (15-Ag). The procedure was same as that of **13-Pd**. **4a** (50.0 mg, 0.062 mmol), 4-nitrophenylacetylene (36 mg, 0.24 mmol), dichloro-bis(triphenylphosphine)palladium (5.0 mg, 7.1 μmol), dichloro-bis(triphenylphosphine)-nickel (5.0 mg, 7.6 μmol), copper iodide (3.0 mg, 16 μmol), triethylamine (66 μL), and distilled toluene (25 mL) as solvent were used. The reaction mixture was stirred for 2 h at 90 °C under argon. Recrystallization from CH_2Cl_2–methanol afforded a violet crystal of **15-Ag** (8 mg) in 15% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.80 (dd, J=4.0, 1.6 Hz, 1H), 8.61–8.46 (m, 5H), 8.21–8.05 (m, 6H), 7.75–7.56 (m, 12H), 7.44 (d, J=8.7 Hz, 2H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 666 (3.65), 617 (3.38), 577 (3.79), 533 (3.88), 467 (4.92), 398 (4.41). HRMS: calcd for $C_{52}H_{30}N_4AgO_2$ [M^++1], 864.1529; found 864.1546.

4.1.15. 3-(4′-Nitrophenylethynyl) NCTPP palladium(II) complex (15-Pd). The procedure was almost same as that of **13-Pd**. **4a** (15.96 mg, 20 μmol), 4-nitrophenylacetylene (2.94 mg, 20 μmol), dichloro-bis(triphenylphosphine)palladium (2.51 mg, 4 μmol), copper iodide (3.86 mg, 20 μmol), triethylamine (3 mL), and distilled toluene (5 mL) as solvent were used. The reaction mixture was stirred for 20 h at room temperature under argon atmosphere. Recrystallization from CH_2Cl_2–methanol afforded a dark-purple crystal of **15-Pd** (3.4 mg) in 20% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 9.74 (s, 1H), 8.18 (d, J=9.0 Hz, 2H), 7.53–7.92 (m, 25H), 7.36 (d, J=8.7 Hz, 2H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 883 (3.43), 791 (3.54), 719 (3.33), 619 (4.54), 577 (4.13), 473 (4.92), 354 (4.57). HRMS: calcd for $C_{52}H_{30}N_5PdO_2$ [M^+], 863.1513; found 863.1419.

4.1.16. 3-Phenyl NCTTP (17). **9** (3.36 mg, 3.9 μmol) was dissolved in THF (2 mL) and the solution of $NaBH_4$ in ethanol (2 mL) was added and the resulting solution was stirred for 1 h. To the reaction mixture, CH_2Cl_2 (20 mL) was added and washed twice with water. The organic phase was separated, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluted with 3% methanol in CH_2Cl_2. The second green fraction containing **17** was evaporated and the residue was recrystallized from CH_2Cl_2–MeOH to afford a violet crystal of **17** (2.0 mg) in 70% yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.82 (m, 2H), 8.40 (m, 6H), 7.66 (d, J=8.4 Hz, 2H), 7.55 (d, J=7.8 Hz, 4H), 7.42 (m, 3H), 7.00 (m, 4H), 2.68 (s, 6H), 2.67 (s, 3H), 2.39 (s, 3H), −4.56 (s, 1H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 756 (3.91), 597 (3.85), 556 (3.88), 454 (5.06). HRMS: calcd for $C_{54}H_{43}N_4$ [M^++1], 747.3488; found 747.3481.

4.1.17. 3-Phenylethynyl NCTPP (18). **13-Ag** (13 mg, 16 μmol) was dissolved in CH_2Cl_2 (4 mL) and TFA (2.4 mL) was added. The resulting solution was stirred for 1 h at room temperature. To the reaction mixture, CH_2Cl_2 (10 mL) was added and washed twice with water. The organic phase was separated, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel

Table 3. X-ray experimental details of **8**, **9**, **13-Ag**, and **13-Pd**

	8	**9**	**13-Ag**	**13-Pd**
Formula	$C_{45}H_{39}N_4Br\cdot CH_2Cl_2$	$C_{54}H_{39}N_4Ag\cdot 0.75CH_2Cl_2$	$C_{52}H_{31}N_4Ag\cdot CH_2Cl_2\cdot CH_3OH$	$C_{52}H_{32}N_4Pd\cdot CH_2Cl_2$
FW	791.60	915.5	936.69	903.18
Color	Violet	Violet	Green	Green
Habit	Prism	Prism	Prism	Prism
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a, Å	11.6334(2)	13.607(5)	12.274(3)	12.636(6)
b, Å	12.903(2)	13.714(5)	13.310(3)	13.264(7)
c, Å	13.1871(2)	13.727(5)	14.803(3)	13.789(7)
α, deg	90.244(6)	60.49(3)	71.282(4)	81.56(4)
β, deg	106.869(6)	73.34(3)	80.678(3)	65.06(4)
γ, deg	111.772(5)	75.44(4)	63.300(3)	86.21(4)
V, Å^3	1745.2(2)	2116(1)	2045.6(7)	2072(1)
Z	2	2	2	2
Radiation (λ, Å)	Mo (0.7107)			
T, °C	−150.0	−150.0	−170.0	−150.0
D_c, g/cm^3	1.506	1.436	1.521	1.447
μ, cm^{-1}	13.76	6.14	6.702	6.200
R_1 (obsd data)	0.087	0.070	0.096	0.085
wR_2 (obsd data)	0.072	0.080	0.104	0.112
GOF	0.984	1.02	1.013	1.055
Independ refs	7374	5716	10,630	8979
Observed refs	1796	2746	3993	4478
Parameters	253	589	434	479

eluted with 2% methanol–CH_2Cl_2. The red fraction containing **18** was collected and the solvent was removed. The residue was recrystallized from CH_2Cl_2–methanol to afford a violet crystal of **18** (6.2 mg) in 54% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.84 (d, J=5.1 Hz, 2H), 8.43–8.51 (m, 4H), 8.37 (d, J=6.3 Hz, 2H), 8.31 (d, J=6.6 Hz, 2H), 8.11 (m, 4H), 7.73–7.84 (m, 12H), 7.23–7.27 (m, 5H), −4.70 (s, 1H). UV/vis (CH_2Cl_2): λ_{max} [nm] (log ε) 767 (3.93), 557 (4.16), 465 (5.05). HRMS: calcd for $C_{52}H_{35}N_4$ [M^++1], 715.2862; found 715.2816.

4.2. X-ray structures

Crystallographic details are summarized in Table 3. Compound **8**: crystals were obtained from CH_2Cl_2–methanol mixed solvent and the crystal was a green prism of approximate dimensions 0.10×0.10×0.10 mm ($C_{45}H_{39}N_4Br\cdot CH_2Cl_2$). Data were collected on a Rigaku R-axis diffractometer in the scan range $\theta\leq 27.5°$. Of the 12,563 reflections measured, 7374 were unique and 1796 had $F_0>3\sigma F_0$. As the number of the observed reflections is small, all atoms of **8** except Br are refined isotropically. Complex **9**: crystals were obtained from CH_2Cl_2–methanol mixed solvent and the crystal was a green prism of approximate dimensions 0.20×0.10×0.10 mm ($C_{54}H_{39}N_4Ag\cdot 0.75CH_2Cl_2$). Data were collected on a Rigaku R-axis diffractometer in the scan range $\theta\leq 27.5°$. Of the 7378 reflections measured, 5716 were unique and 2746 had $F_0>3\sigma F_0$. Complex **13-Ag**: crystals were obtained from CH_2Cl_2–methanol mixed solvent and the crystal was a green prism of approximate dimensions 0.30×0.10×0.10 mm ($C_{52}H_{31}N_4Ag\cdot CH_2Cl_2\cdot CH_3OH$). Data were collected on a Bruker APEX diffractometer in the scan range $\theta\leq 27.5°$. Of the 29,024 reflections measured, 10,630 were unique and 3993 had $F_0>3\sigma F_0$. Complex **13-Pd**: crystals were obtained from CH_2Cl_2–methanol mixed solvent and the crystal was a green prism of approximate dimensions 0.40×0.10×0.10 mm ($C_{52}H_{32}N_4Pd\cdot CH_2Cl_2$). Data were collected on a Rigaku R-axis diffractometer in the scan range $\theta\leq 27.5°$. Of the 17,940 reflections measured, 8979 were unique and 4478 had $F_0>3\sigma F_0$. In the crystal of **13-Pd**, the confused pyrrole is in disorder and located equally on the N1- and N3-pyrrole. Thus, the phenylethynyl group appears at both C3 and C32 with 0.5 occupancy. In addition, the vacant space formed by the disorder of the phenylethynyl group is occupied by a CH_2Cl_2 molecule. Owing to this complicated disorder in the crystal, the atom-positions of the phenylethynyl group are not exactly determined. The structures were solved by direct methods and refined by full-matrix least-square procedures. The hydrogen atoms were calculated in ideal positions. Solution and structure refinement calculations for the structures were performed using the teXsan crystallographic package of Molecular Structure Corporation. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with reference number CCDC 638674–638677 for **8**, **9**, **13-Ag**, and **13-Pd**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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