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Letter

Porphyriynes: 18-π-Conjugated Macrocycles Incorporating a Triple Bond

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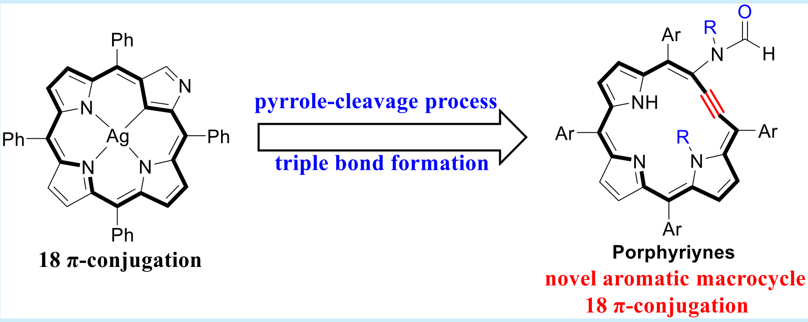

ABSTRACT: Tetraphenylporphyriyne (**Pyne1**), a novel porphyrin analogue with a C≡C bond incorporated into an 18-π-conjugated system, has been created via cleavage of the N-confused pyrrolic ring in Ag(III) N-confused tetraphenylporphyrin. The structure of **Pyne1** was confirmed by X-ray crystallography and ^{1}H NMR, IR, and UV−vis spectroscopy. The mechanism of cleavage of the N-confused pyrrolic ring was investigated by theoretical calculations. The successful synthesis of other **Pynes** indicated the generality of this protocol.

Porphyrins and their analogues constitute an important class of π-conjugated macrocycles and garner extensive research attention because of their unique structural and optical properties and their wide applications in catalysis, medicine, materials, and supramolecular chemistry.[1] Different from naturally occurring porphyrins and hydroporphyrins, which have an 18-π-electron aromatic system based on the tetrapyrrolic framework, synthetic porphyrinoids containing at least one non-pyrrolic unit, termed "pyrrole-modified porphyrins" (PMPs),[2] such as carbaporphyrins, heteroporphyrins, vacataporphyrins, X-confused porphyrins (X = NH, O, S), neoconfused porphyrins, and porphyrinoids bearing different heterocyclic moieties with the NNNN core preserved (Figure 1), have been created and extensively studied. It is worth noting that Latos-Grażyński reported the novel contracted heteroporphyrinoids dithiaethyneporphyrin and dithiaethyneazuliporphyrin, which have a triple bond embedded in the macrocyclic skeleton but retain their macrocyclic aromaticity through an 18-π-electron delocalization pathway (Figure 1).[3]

"Breaking and mending" is the most popular strategy to access PMPs from porphyrins. It usually involves a pyrrole-cleavage step and thus yields a series of novel porphyrinoids lacking a pyrrolic ring, such as secochlorins[4] and chlorophins.[5] In 1992, Chang reported the first synthesis of a pyrrolic-ring-lacking macrocycle, secochlorin, which was accessed by an unexpected oxidative ring-opening of an (octadehydrocorrinato)nickel(II) salt.[4a] Thereafter, Bonnett,[4b,c] Dolphin,[4d] Sessler,[4e] and Richeter[4f] each developed a series of novel secochlorins. In 1999, Dolphin and Brückner reported the synthesis of the first nickel(II) chlorophin via the rhodium-mediated stepwise decarbonylation of secochlorin.[5a] Brückner has also devoted a great deal of effort to converting secochlorins into other PMPs.[5b,6] Our group previously established a convenient route to chlorophins and bacteriophins through the degradation of nickel(II) 2,3,12,13-tetrabromo-5,10,15,20-tetraarylporphyrins under the action of (E)-benzaldoxime anion.[5c] These novel nickel(II) bacteriophins are porphyrin analogues lacking two pyrrolic rings that show intense absorptions in the near-IR region, making them potential photosensitizers for photodynamic therapy. In 2017, Kim and Osuka extended this methodology to subporphyrins and successfully synthesized the first boron(III) subchlorophin,[7] the optical and electronic properties of which can be tuned through peripheral modifications. Accordingly, while many PMPs with distinct structures and optical properties have

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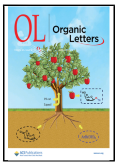

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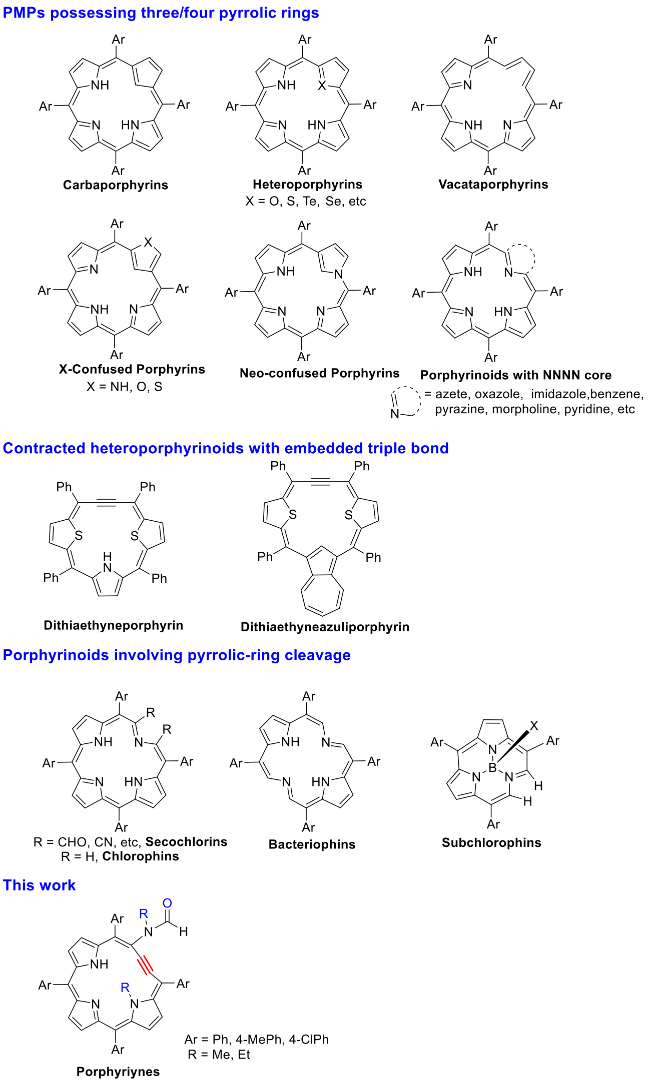


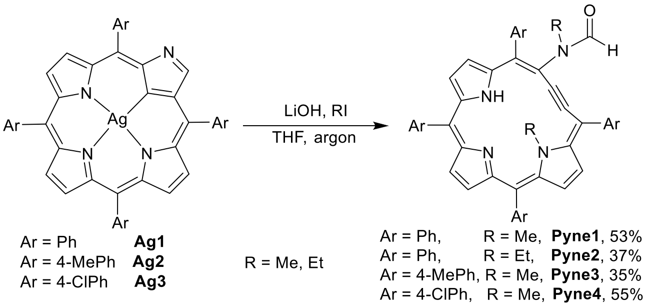
Figure 1. Selected structures of PMPs.

been created, there is ongoing interest in the synthesis and structures of new PMPs.

N-Confused porphyrins (NCPs), which were first reported independently by Furuta[8] and Latos-Grażyński[9] in 1994, are isomers of regular porphyrins. NCPs have aroused significant research attention in recent decades because of their distinct structural, physical, chemical, and coordination properties, all of which are quite different from those of regular porphyrins. Previous studies have revealed that the peripheral 2-*N* and 3-*C* positions and the C═N bond as well as the inner 21-*C* position are active in NCPs.[10] However, the creation of new PMPs via cleavage of the pyrrolic ring in NCPs remains unexplored. We have reported that alcohols undergo nucleophilic addition with Ag(III) NCPs to give *C*-3-alkoxylated Ag(III) NCPs,[11] supporting the conclusions of computational analysis, which indicated that the C═N bond on the periphery of Ag(III) NCPs is partially isolated from the 18-π-electron macrocyclic conjugation system and is the active electrophilic center. Accordingly, we envisioned that the N-confused pyrrolic ring in Ag(III) N-confused tetraphenylporphyrin (**Ag1**) might be cleaved under attack by certain strong nucleophiles. Herein we report the synthesis, structure, and optical properties of porphyriynes (**Pynes**), novel 18-π-electron aromatic macrocyclic compounds that incorporate a triple bond.

Initially, we treated **Ag1** with LiOH in THF at room temperature and observed that the color of the reaction solution changed from brown to green. However, TLC indicated a complex mixture. We reasoned that certain intermediate(s) is/are generated in this reaction and that major product(s) may be obtained if the intermediate(s) could be captured. Optimal reaction conditions were established after screening of the effects of numerous variables, including the nucleophile, solvent, concentration, and temperature (see Tables S1 and S2 for details). Of the nucleophiles tested, which were LiOH, Li_2CO_3, NaOH, and *n*-BuLi, only LiOH gave the desired product. We believe that both the lithium cation and hydroxide are essential for this transformation, where the lithium cation coordinates to the C═N nitrogen and facilitates nucleophilic attack of the hydroxide. To our delight, treatment of 72 mg of **Ag1** with 40 equiv of LiOH and 2 mL of CH_3I in 12 mL of THF at room temperature for 24 h afforded the bright-green compound **Pyne1** in 53% yield. To examine the generality of this synthetic protocol, three Ag(III) N-confused tetraarylporphyrins (**Ag1**, **Ag2**, and **Ag3**) were treated under similar reaction conditions and trapped with methyl iodide or ethyl iodide. The desired products **Pyne2−4** were obtained in moderate yields (Scheme 1).

Scheme 1. Synthesis of Pynes from Ag(III) NCPs



The ^1H NMR spectrum of **Pyne1** in $CDCl_3$ shows two $-CH_3$ signals at 3.77 and −3.88 ppm, which indicates that one methyl group has been introduced into the periphery and the other methyl group has been introduced into the inner core of the macrocycle. Six β proton signals are observed as doublets, and they are shifted upfield slightly compared with those for N-confused tetraphenyl porphyrin (**NCTPP**). The chemical shift of the phenyl proton in **Pyne1** is similar to that of **NCTPP**. When the ^1H NMR spectrum of **Pyne1** is recorded in DMSO-*d*$_6$, a broad peak appearing at −0.06 ppm is observed, indicating a proton attached to the inner N atom. HMQC and $^1H-^1H$ COSY analyses allowed the signal at 8.85 ppm to be assigned to the proton on the amide group. The ^{13}C NMR spectrum (recorded in CD_2Cl_2) shows no resonance relevant to the normal acetylene carbon in the range 70−95 ppm, most likely due to the includsion of the acetylene carbon as part of a large conjugated system and/or the existence of the cumulene canonical structure.[3] We propose that there are two possible canonical structures (each canonical structure has two tautomers) for **Pyne1** that contribute to the 18-π-electron macrocyclic delocalization (Scheme 2) in solution, and the acetylenic character of the $C_{sp}-C_{sp}$ moiety dominates (see the NMR Analysis section in the Supporting Information for

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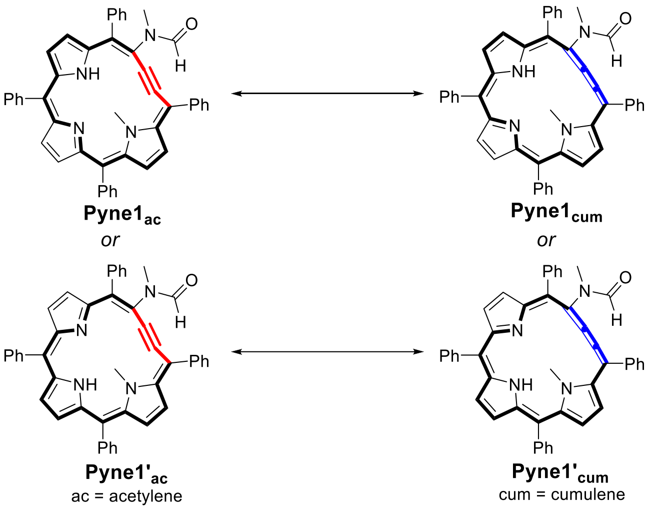
Scheme 2. Canonical Structures of Pyne1



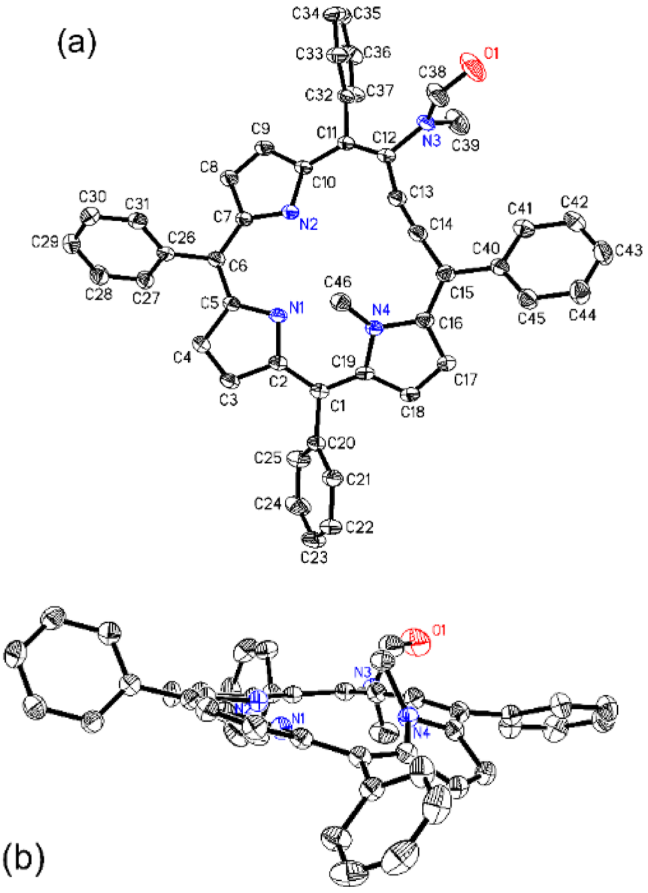


Figure 2. X-ray structure of **Pyne1**: (a) top view; (b) side view. The solvent molecules and hydrogen atoms have been omitted for clarity. The thermal ellipsoids are scaled to 30% probability.

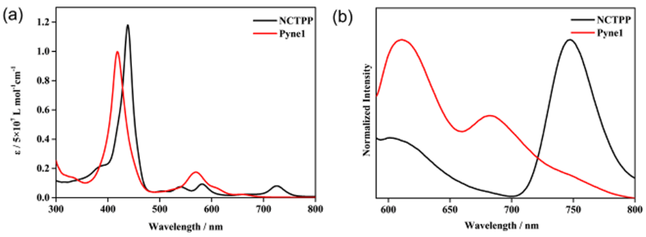


Figure 3. (a) Absorption spectra of **Pyne1** and **NCTPP** at a concentration of 5 × 10^{-7} M in CH_2Cl_2. (b) Emission spectra of **Pyne1** and **NCTPP** at a concentration of 5 × 10^{-7} M in CH_2Cl_2 (excited at 570 nm).

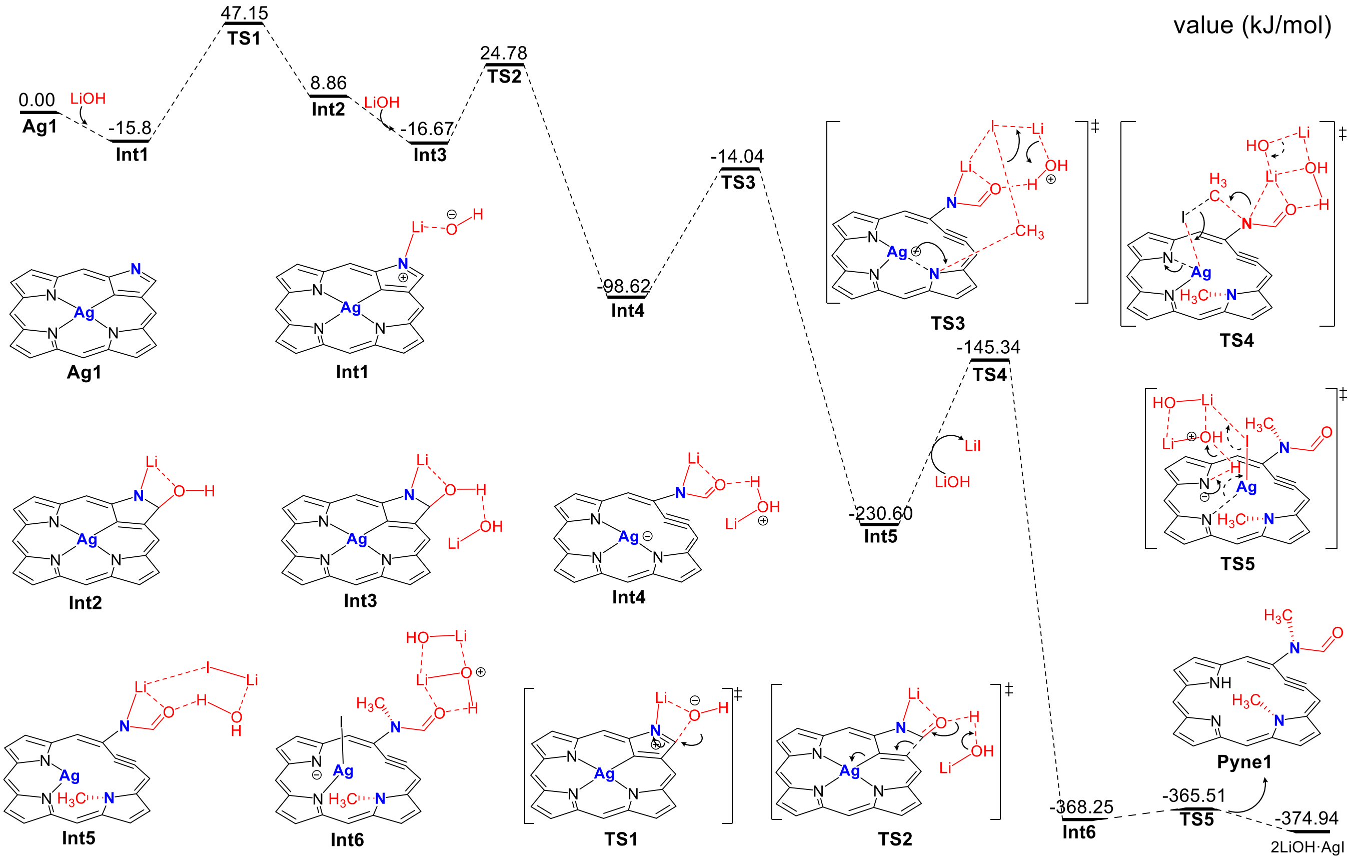
details). MALDI-MS analysis of **Pyne1** revealed a parent ion peak at $m/z = 659.2809$ (calcd for $C_{46}H_{35}N_4O = 659.2805$, $[M + H]^+$), suggesting the removal of Ag and the introduction of oxygen. IR analysis showed a characteristic peak at 1674 cm^{-1}, which indicates the presence of an amide group in the structure.

To our delight, crystals of **Pyne1** were obtained by slow evaporation of a chloroform/methanol solution of **Pyne1** at room temperature. Its definitive structure was then determined by single-crystal X-ray diffraction analysis, which clearly showed that the N-confused pyrrolic ring has been cleaved (see Figure 2 and Table S3). Intriguingly, a C≡C bond is observed in the macrocycle. The skeleton of this macrocycle is distorted by the introduction of a methyl group onto N4. The C−C and C−N bond lengths within the macrocyclic skeleton are reasonable for a π-conjugated system. The C13−C14 bond distance is 1.221(3) Å, which is much shorter than those of the other C−C bonds, indicating that C13 and C14 are connected by a triple bond. The H2···N1 distance is 2.55 Å, implying that there is an intramolecular hydrogen bond (N2−H2···N1). The distances of N4, C17, and C18 from the mean macrocycle plane (see Figure S1 and Table S4) are 0.3508, −0.7954, and −0.9225 Å, respectively, indicating that the methylated pyrrole ring is very strongly deviated from the mean macrocycle plane. The C14−C15−C16−N4 and C2−C1−C19−N4 torsion angles are −23.5° and 20.4°, respectively, also revealing that the pyrrolic ring is strongly deviated from the macrocycle plane. Since **Pyne1** is less planar than **NCTPP**, it may have a weaker conjugation system. More obviously, the cavity of **Pyne1** is occupied by the N4-methyl group, which hinders the coordination of **Pyne1** to metal ions such as Ni^{2+}, Ag^+, Co^{2+}, and Cu^{2+}.

The absorption and emission spectra of **Pyne1** are shown in Figure 3. In the absorption spectrum (Figure 3a), the maximum of the B band appears at 418 nm, and three Q bands appear at 569, 610, and 657 nm. Compared with **NCTPP**, **Pyne1** exhibits a hypsochromic shift of the absorption maxima and different Q-band curves, indicating that cleavage of the N-confused pyrrole unit alters its electronic transitions. The absorption spectra of **Pyne1** recorded in solvents with different polarities show no obvious differences in the Q-band region (see Figure S3), indicating that the Q-band originates from a localized electronic transition with little charge transfer character. This also indicates that both transitions are π−π* transitions within the novel 18-π-electron conjugation system. The emission spectrum of **Pyne1** shows an emission peak of the lowest energy at 680 nm, which is shifted hypsochromatically compared with that of **NCTPP** at 748 nm (Figure 3b).

Pyne1 and **NCTPP** were subjected to TD-DFT analysis at the PBE0/6-31G* level to better understand their electronic structures (see the Theoretical Calculations section in the Supporting Information for details). The calculated and experimental absorption spectra match well. The B band absorption of **Pyne1** originates from a mixed transition from HOMO−1 to LUMO and HOMO−1 to LUMO+1, and the Q-band absorptions of **Pyne1** correspond to mixed transitions from HOMO to LUMO and HOMO to LUMO+1. The

Scheme 3. Proposed Mechanism and Calculated Results for the Formation of Pyne1



calculated S_1 transition of **Pyne1** is at 578 nm, which is higher in energy compared with that of **NCTPP** (629 nm); this explains the hypsochromic shift of **Pyne1** compared with **NCTPP** in both absorption and emission. The aromaticities of **Pyne1** and **NCTPP** were calculated at the same level (see the Supporting Information). Many descriptors of **Pyne1**, such as NICS(0),[12] NICS(1),[12] HOMA,[13] FLU,[14] and ICSS,[15] resemble that of **NCTPP**, indicating that the 18π conjugation is maintained after cleavage of the N-confused pyrrolic ring. The ACID[16] profiles show clockwise ring currents in **Pyne1**, indicating the aromaticity of the triple-bond-containing 18π macrocyclic skeleton.

According to previous studies on the NH tautomerism of free-base NCP[17] and the resonance structures of Ni(II) NCP,[18] the peripheral C═N bonds of some tautomer of free-base NCP and Ni(II) NCP could be considered as isolated from the 18-π-electron-conjugated aromatic system. Accordingly, we examined the reactivities of free-base NCP and Ni(II) NCP under the same conditions, but no desired product was obtained. Previous studies have revealed that the inner 21-C position of Ni(II) NCP[19] and free-base NCP[20] is very active, which may explain why the reactivities of free-base NCP and Ni(II) NCP are different from that of Ag(III) NCP. Theoretical calculations also indicated that the Ag(III) NCP scaffolds are critical to the successful construction of **Pynes**. A plausible reaction mechanism is illustrated in Scheme 3 (for details, see Scheme S2 and the Detailed Calculation Results section in the Supporting Information). First, **Ag1** reacts with LiOH to form **Int1**, which undergoes C−O bond formation to give **Int2** via **TS1**. Intermolecular-hydrogen-bond formation between **Int2** and another LiOH leads to **Int3**, which readily undergoes a sequential transformation comprising C−C bond cleavage, triple bond formation, and Ag(III) reduction to give **Int4**. In **Int4**, one of the nitrogen atoms in the inner core becomes a nucleophilic site and attacks CH_3I to produce **Int5** via the formation of **TS3**. Further nucleophilic reaction of the peripheral nitrogen atom with another CH_3I and another LiOH provides **Int6**, which undergoes proton transfer followed by demetalation to deliver the final product **Pyne1**. This mechanism also explains the need for excess LiOH and CH_3I in the reaction.

In summary, **Pynes** are novel porphyrinoids with a C≡C bond in an 18-π-conjugated skeleton, and they are the first examples of PMPs created by cleavage of the N-confused pyrrolic ring of NCPs. The structure of **Pyne1** has been confirmed by X-ray crystallography. **Pynes** exhibit spectroscopic properties similar to those of NCPs and porphyrins. The electronic structure and aromaticity of **Pyne1** were fully investigated by theoretical calculations. We propose that the Ag(III) NCP scaffold plays a vital role in the N-confused-pyrrolic-ring-cleavage process. The synthetic protocol was demonstrated to be effective for constructing other **Pynes** with different substitutional groups. Further studies of the properties and derivatization of **Pynes** are ongoing in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c00356.

General information, synthesis, X-ray crystallography, UV−vis absorption spectra, theoretical calculations, and NMR spectra (PDF)

Accession Codes

CCDC 834814 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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