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Synthesis of *meso,meso′*-Pyrrole-Bridged Diporphyrins by Cu(I)-Mediated Annulation

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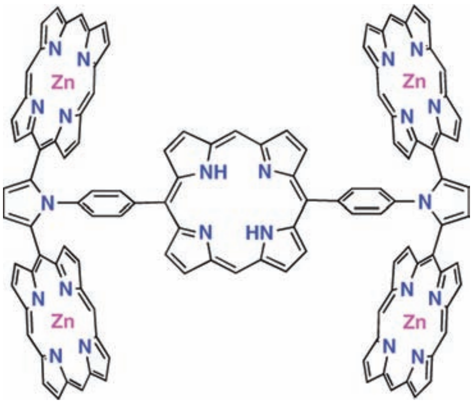
ABSTRACT



Cu(I)-mediated annulation of *meso,meso′*-1,3-butadiyne-bridged Zn(II) diporphyrin with various amines efficiently provided *meso,meso′*-pyrrole-bridged Zn(II) diporphyrins. Notable intramolecular electronic interactions in these diporphyrins were observed. A starburst porphyrin pentamer was synthesized via Suzuki−Miyaura coupling of *N*-bromophenylpyrrole-bridged diporphyrin and *meso,meso′*-diborylated porphyrin.

Both cyclic and acyclic porphyrin arrays have been extensively studied in view of mimicry of natural photosynthesis, applications to molecular wires, and nonlinear optical devices.[1] Porphyrin dimers linked by various spacers have been synthesized as a fundamental structural motif to investigate the electronic interactions between the porphyrins, which will influence their electrochemical and photophysical properties.[2] Such porphyrin dimers are often prepared by oxidative coupling reactions or metal-catalyzed coupling reactions.[3,4]

Acetylene moieties can be selectively activated by transition metal catalysts, hence allowing site-selective reactions to provide heterocyclic compounds.[5] However, this type of reaction has been rarely used for *meso*-ethynylated porphyrins, while such species have been actively studied in light of their highly conjugated electronic properties.[6,7] Recently

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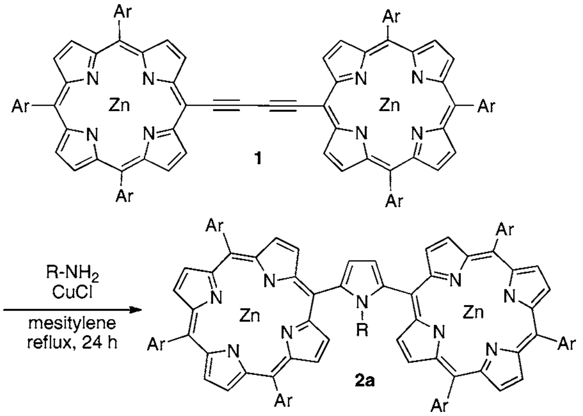
we have explored the transition-metal-catalyzed annulation reactions of *meso*-ethynylated porphyrins that effectively provide 5-azaindole- and 1,2,3-triazole-appended porphyrins.[7] Here we report Cu(I)-mediated annulation of 1,3-butadiyne-bridged diporphyrin with various amines, which provides pyrrole-2,5-bridged diporphyrins in moderate to good yields.[8,9] Although a pyrrole moiety is quite attractive as a bridging spacer in view of the electron-rich property, effective conjugation, and potential use as a hydrogen-bonding donor, handling of pyrroles is not trivial because of their instability and high reactivity. Hence this annulation approach, which circumvents functionalization of pyrroles, is useful from a synthetic viewpoint.

Several synthetic procedures for the transformation of 1,3-diynes to pyrrole rings have been reported.[10,11] We modified the reaction conditions of the Cu(I)-mediated annulation[10] so as to be applicable for the porphyrin system. A mesitylene solution of 1,3-butadiyne-bridged diporphyrin **1**, aniline (50 equiv), and CuCl (4 equiv) was refluxed for 24 h (Scheme 1). After chromatographic separation, *N*-phenylpyrrole-bridged diporphyrin **2a** was obtained in 56% yield. The structure of **2a** has been confirmed by the spectroscopic data and single crystal X-ray diffraction analysis. High-resolution electro-spray-ionization time-of-flight (HR-ESI-TOF) mass spectrum detected the parent ion peak of **2a** at m/z = 2017.0547 (calcd for $C_{134}H_{150}N_9Zn_2$ $[M + H]^+ = 2017.0598$). The ^1H NMR spectrum of **2a** is fully consistent with its structure, where the pyrrolic β-protons are observed at $\delta = 7.76$ ppm, and the phenyl protons at the pyrrole bridge are shifted upfield at $\delta = 6.83$, 5.59, and 5.57 ppm as a result of the ring current of the porphyrins. Slow vapor diffusion of acetonitrile to a dioxane solution of **2a** provided its nice crystals for X-ray diffraction analysis. The crystal structure of **2a** revealed unambiguously a *N*-phenylpyrrole-bridged diporphyrin skeleton, in which the Zn−Zn center-to-center distance is 11.4 Å, the dihedral angle between the pyrrole bridge and the porphyrin mean plane is 79°, and that between the two porphyrin planes is 135° (Figure 1).[12]

Scheme 1. Synthesis of **2a**[a]



[a] Ar = 3,5-di-*tert*-butylphenyl, R = Ph.

Figure 1. X-ray crystal structure of **2a**. *meso*-Aryl groups and hydrogen atoms are omitted for clarity. The thermal ellipsoids were at 50% probability level.

This annulation reaction was investigated for various amines (Table 1). The reaction of *p*-methoxy- and *p*-bromoanilines provided the corresponding diporphyrins **2b**

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(12) **Crystallographic data for 2a.** Formula: $C_{134}H_{149}N_9Zn_2$, M_w = 2016.36, monoclinic, space group$C2/c$, $a = 29.021(5)$, $b = 10.712(5)$, $c = 49.322(5)$ Å, $\beta = 98.552(5)°$, $V = 15162(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.883$ g cm^{-3}, $T = -183$ °C, 6626 measured reflections, 13315 unique reflections ($R_{int} = 0.0930$), $R_1 = 0.0930$ ($I > 2\sigma(I)$), $wR_2 = 0.2347$ (all data), GOF = 0.930. The contribution to the scattering arising from the presence of the disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package: (a) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, 2005. (b) Sluis, P.; van der; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201.

Table 1. Synthesis of Pyrrole-Bridged Diporphyrins[a]

entry	R	product	yield (%)[b]
1	Ph	**2a**	56
2	4-MeO(C_6H_4)	**2b**	74
3	4-Br(C_6H_4)	**2c**	79
4	mesityl	**2d**	15
5	benzyl	**2e**	31
6	octyl	**2f**	25

[a] Reaction conditions: **1** (5 μmol), amine (50 equiv), CuCl (4 equiv), in mesitylene (1 mL), reflux, 24 h. [b] Isolated yield.

and **2c** in good yields, while bulky 2,4,6-trimethylaniline and alkylamines were found to be less reactive. These synthesized pyrrole-bridged diporphyrins were fully characterized by their spectroscopic data (Supporting Information).

The butadiyne-bridged diporphyrin **1** shows the perturbed and red-shifted UV−vis absorption spectrum.[13] Compared with this, the absorption spectrum of **2a** exhibits a split and blue-shifted Soret band at 426 and 436 nm and Q-bands at 556 and 601 nm (Figure 2), reflecting the decreased electronic interactions of the *meso*-bridged pyrrole spacers. The fluorescence spectrum of **2a** is observed at 613 and 653 nm with a clear vibronic structure. While the absorption and fluorescence spectra of **2b** and **2c** are similar to those of **2a**, the fluorescence spectrum of **2d** that bears a sterically hindered *N*-pyrrole aryl substituent is red-shifted at 630 nm. Interestingly, the fluorescence spectra of **2e** and **2f** that bear *N*-pyrrole alkyl substituents are broader and red-shifted, as compared with those of *N*-aryl-substituted diporphyrins. The fluorescence quantum yields of **2e** and **2f** are almost twice as those of **2a**−**2c** (Table 2).

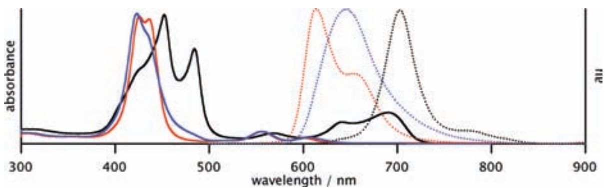


Figure 2. UV−vis absorption (left) and fluorescence (right) spectra in $CHCl_3$ (black line = **1**, red line = **2a**, blue line = **2e**). The excitation wavelengths are 452 nm for **1**, 426 nm for **2a**, and 423 nm for **2c**.

Table 2. Photophysical Data

compound	λ_A (nm)[a]	λ_F (nm)	Φ_F[b]
2a	426, 436	613, 653	0.052
2b	426, 436	613, 655	0.065
2c	429, 437	613, 655	0.066
2d	428, 438	630	0.073
2e	423, 433[c]	645	0.120
2f	422, 432[c]	648	0.128

[a] Soret bands. [b] Quantum yields were determined with reference to the value (0.033) of Zn(II)TPP in toluene. [c] Shoulder.

The electrochemical properties of **2a**, **2c**, and **2f** were investigated by cyclic voltammetry. Characteristically, the first oxidation waves were split into two waves in all cases (Figure 3), indicating the substantial electronic interaction between the two porphyrins through the pyrrole spacer. The splitting potential widths are similar, being 0.08−0.09 V. In addition, the oxidation potentials are dependent on the *N*-substituent on the central pyrrole: 0.27, 0.30, and 0.32 V for **2f**, **2a**, and **2c**, respectively. This is due to the presence of the electronic communication between the porphyrin and the pyrrole spacer, while such dependence is weaker for the reduction potentials.

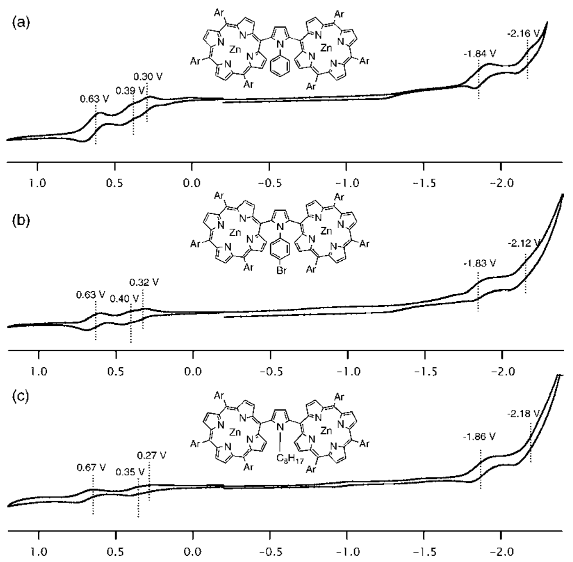
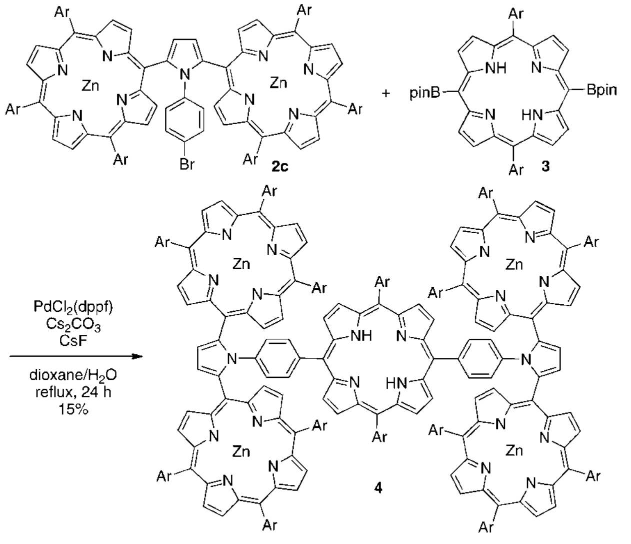


Figure 3. Cyclic voltammograms of (a) **2a**, (b) **2c**, and (c) **2f**. (solvent, CH_2Cl_2; supporting electrolyte, Bu_4NPF_6 (0.10 M); counter electrode, Pt; reference electrode, Ag/Ag^+; scan rate, 0.05 V/s). Accurate potentials were determined by the differential pulse voltammetry method (Supporting Information).

We then anticipated that *N*-bromophenyl Zn(II) diporphyrin **2c** would be used as a building block of large and more elaborated multiporphyrin arrays. Thus, we examined the Suzuki−Miyaura cross-coupling reaction of **2c** with diborylated porphyrin **3**, which furnished starburst Zn(II)-free-base hybrid porphyrin pentamer **4** in 15% yield (Scheme 2).[14] The MALDI-TOF mass measurement detected the parent ion peak at $m/z = 4715$ (calcd for $C_{316}H_{347}N_{22}Zn_4$ $[M - H]^- = 4715$). The ^{1}H NMR spectrum of **4** elucidated its highly symmetric structure, exhibiting the pyrrolic β-protons of the central free base moiety at $\delta = 7.33$ and 6.38 ppm (Figure S15 in Supporting Information). This result demonstrates that *meso,meso′*-pyrrole-bridged diporphyrins are stable enough to be used for transition-metal-catalyzed coupling reaction.

Figure 4 shows the UV−vis absorption and fluorescence spectra of **2a** and **4**, along with *meso*-tetraphenyl porphyrin (TPP). The absorption spectrum of **4** is almost the superposition of those of **2a** and TPP in a 2:1 ratio, allowing a selective excitation at both Zn(II) porphyrins. The fluorescence spectrum of **4** upon selective excitation of the Zn(II) porphyrin parts at 436 nm is practically the same as that of TPP with a small shoulder at 620 nm, indicating the efficient

Scheme 2. Synthesis of Porphyrin Pentamer **4**



intramolecular excitation energy transfer from the zinc(II) porphyrin peripheries to the free-base porphyrin core. The fluorescence quantum yield of the pentamer **4** is 7.2%, which is larger than that of **2a** (5.2%). This result again indicates the efficient intramolecular excitation energy transfer from the Zn(II) porphyrin peripheries to the free-base TPP core.

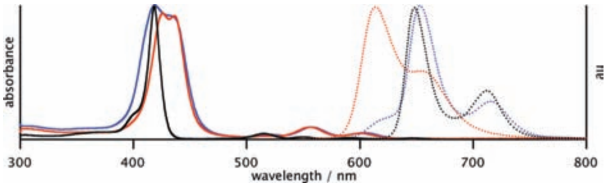


Figure 4. UV−vis absorption (left) and fluorescence (right) spectra in CHCl$_3$ (blue line = **4**, red line = **2a**, black line = TPP).

In summary, we have synthesized *meso,meso′*-pyrrole-bridged zinc(II) diporphyrins via the Cu(I)-mediated annulation reaction of *meso,meso′*-1,3-butadiyne-bridged diporphyrin with various amines. In these diporphyrins, notable electronic interactions are observed in the absorption and fluorescence spectra as well as the cyclic voltammograms, which vary upon the pyrrolic *N*-substituent. In Zn(II)-free-base hybrid porphyrin pentamer **4**, synthesized by the Suzuki−Miyaura coupling reaction of **2c** and **3**, the energy transfer from the Zn(II) porphyrin peripheries to the free-base porphyrin core takes place efficiently. Extension of this synthetic strategy to more elaborated pyrrole- or heterocycle-bridged multiporphyrin arrays is actively pursued in our laboratory.

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Supporting Information Available: Experimental procedures, compound data, and crystallographic data for **2a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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