Porphyrinoids

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Unique Interaction between Directly Linked Laminated π Planes in the Benzonorrole Dimer**

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Interactions between two π planes are an important subject for study because they are ubiquitous and often play important roles in functional molecules.[1] In particular, the interaction between porphyrins and related macrocycles have gathered much attention because of its crucial role in biochemistry as well as materials science.[2] To study the interaction between porphyrinoids, the connection of two π planes would be one of the most straightforward strategies. In the dimers having a direct covalent linkage, two π planes are usually arranged in a side-by-side manner to form tapelike structures.[3] In contrast, the laminated face-to-face dimers having a direct covalent linkage are rarely reported, plausibly because of the lack of an efficient synthetic methodology (Figure 1). Alternatively, the arrangement of π planes in a face-to-face manner can be achieved readily with the help of a rigid bridge or metal coordination, even though the distances between two π planes tend to be long (over 3.7 Å).[4,5] Herein we have successfully constructed directly linked, face-to-face π planes having short π–π distances (less than 3.5 Å) using a corrole isomer, and a unique interaction between the two π planes was observed. To the best of our knowledge, this is the first example in porphyrin chemistry of a directly linked, face-to-face π dimer having shorter π–π distances.

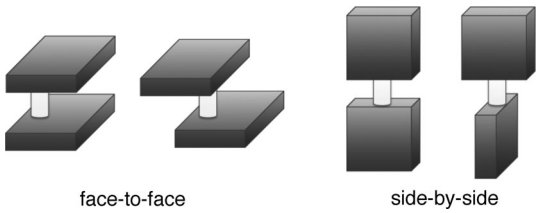

Figure 1. Directly linked π planes.

In the directly linked face-to-face π dimer, we think that the interaction between the two π planes can be discussed based on molecular orbitals. Thus, in analogy to the typical interaction between the two *p* orbitals in ethylene (Figure 2a), bonding and antibonding interactions between two π planes are considered for the face-to-face structure. When almost no orbital interaction exists, bonding and antibonding orbitals will be degenerate, and have almost the same energies as those of the original orbitals (Figure 2b). In contrast, when strong orbital interactions exist, large energy splitting will be observed (Figure 2c).

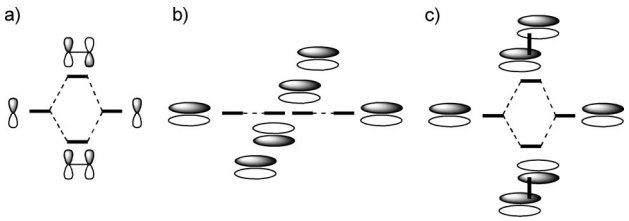

Figure 2. Bonding and antibonding interactions between two orbitals: a) p orbitals, b) non-interacting face-to-face π planes, and c) strongly interacting face-to-face π planes.

For the construction of the directly linked, face-to-face π planes, a member of carbacorrole is utilized, since it has a reactive carbon atom inside the macrocycle and would be appropriate for this purpose. We have recently developed a unique strategy to prepare carbacorroles, namely the N-linked strategy. The N-linked strategy rests on the formation of a N–C bond for macrocyclization (Figure 3). The first example was found during the synthetic study of the N-confused corrole, as the N-linked corrole (named norrole) was isolated accidentally as a by-product.[6] Subsequently, the C-fused norrole was synthesized, and thus suggested the generality of the N-linked strategy as well as the high reactivity of the inner carbon atom.[7] Additionally, Lash and co-workers reported a novel porphyrin isomer possessing

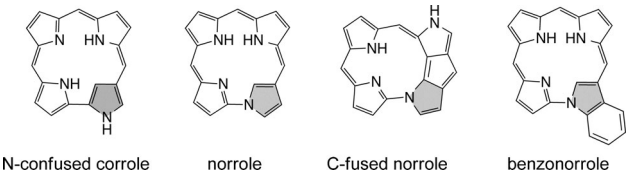

Figure 3. N-Confused corrole and norrole derivatives.

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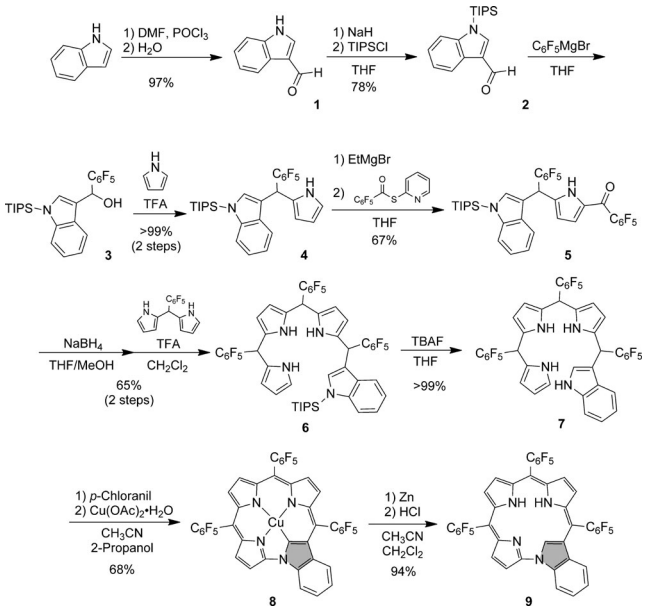
a similar N linkage.[8] Although high reactivity of the N-linked bipyrrole moiety motivated us to use norrole derivatives, the reported synthetic route only gave norrole in a tiny amount and thus an alternative method for the synthesis of norrole derivatives was essential. A simple remedy would be utilization of a substituted pyrrole to block the other reactive site or the formation of an N-confused corrole. Herein an indole was adopted as a substituted pyrrole, such that the target molecule would be benzonorrole.

Synthesis of a benzonorrole precursor, N-confused benzobilane, could be achieved by a strategy similar to that for the synthesis of N-confused bilane (Scheme 1).[6,9] Starting



Scheme 1. Preparation of benzonorrole. TFA = trifluoroacetic acid, THF = tetrahydrofuran, TIPS = triisopropylsilyl.

from indole, formylation and subsequent protection with a triisopropylsilyl group gave **2** in 76% yield (2 steps).[10] The reaction of **2** with C_6F_5MgBr gave carbinol **3**, and subsequent acid condensation with pyrrole afforded the N-confused benzodipyrromethane **4** quantitatively. Then **4** was acylated with *S*-2-pyridyl pentafluorobenzothioate to give the monoacyl derivative **5** in 67% yield. Reduction of **5** and subsequent acid condensation with dipyrromethane gave the N-protected N-confused benzobilane **6** (65% yield, 2 steps). Finally, deprotection of **6** with tetrabutylammonium fluoride (TBAF) gave the N-confused benzobilane **7** quantitatively.

Oxidative cyclization of the N-confused benzobilane **7** was satisfactorily achieved by the aid of copper metal. Upon treatment of **7** with *p*-chloranil and then with $Cu(OAc)_2 \cdot H_2O$, the Cu^{III}/benzonorrole **8** was obtained in 68% yield. Demetallation of **8** by Zn/HCl gave the free-base benzonorrole **9** in 94% yield.[11] The total yield from indole to benzonorrole is 21% (10 steps), which is considerably high among corrole isomers.[12] The structures of **8** and **9** were elucidated by X-ray crystallographic analysis (Figure 4). Complex **8** has a nearly planar conformation. In contrast, the indole ring of **9** sits at

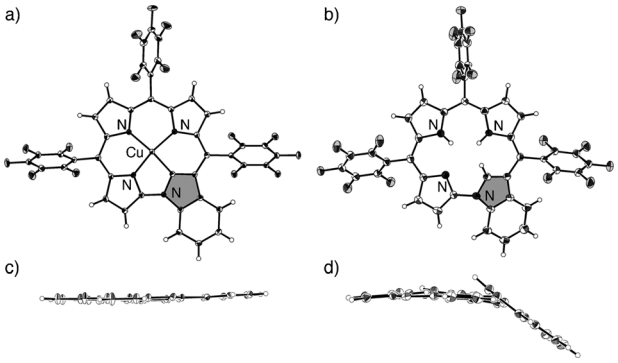
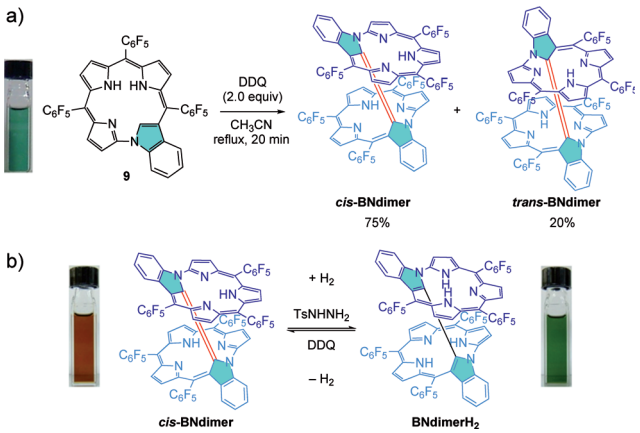


Figure 4. Top and side views of the X-ray structures of **8** (a,c) and **9** (b,d). The *meso*-C_6F_5 groups are omitted for clarity in the side views. Thermal ellipsoids are shwon at the 30% probability level.[16]

a 35.1° angle to the tripyrrane plane, an angle which is significantly larger than that of **8** (3.1°).

The uniqueness of benzonorrole among porphyrinoids became evident when it was further oxidized by 2,3-dichloro-5,6-dicyano-1,4-benozoquinone (DDQ), thus forming the unprecedented directly linked dimers. Upon treatment of **9** with DDQ in CH_3CN at reflux, *cis*-BNdimer and *trans*-BNdimer were obtained in 75 and 20% yields, respectively (Scheme 2a). Both structures were confirmed by X-ray crystallographic analyses. Importantly, the carbon–carbon



Scheme 2. a) DDQ oxidation of **9**. b) Interconversion between *cis*-BNdimer and $BNdimerH_2$. The photos show the color in CH_2Cl_2 solution.

bond lengths between the two benzonorrole units are 1.357(5) and 1.336(3) Å for *cis*-BNdimer and *trans*-BNdimer, respectively, thus suggesting that those bonds are double bonds. Furthermore, reduction of *cis*-BNdimer with $TsNHNH_2$ gave $BNdimerH_2$ quantitatively, and the color of solution changed significantly (Scheme 2b). In the X-ray structure the bond length between the two benzonorrole units is 1.476(3) Å, which is typical for a single bond between two sp^2-carbon atoms.[13] Upon DDQ oxidation, $BNdimerH_2$ reformed *cis*-BNdimer quantitatively. Surprisingly, $TsNHNH_2$ reduction of *trans*-BNdimer did not proceed and never gave the expected reduced product.

Structural parameters for the X-ray structures of $BNdimerH_2$, *cis*-BNdimer, and *trans*-BNdimer are summarized in Figure 5. In $BNdimerH_2$, the two benzonorrole planes are close (3.14 Å) and almost parallel (6.5°) to each other, such

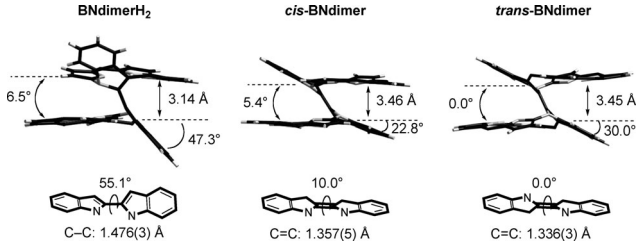


Figure 5. Structural parameters of $BNdimerH_2$, *cis*-BNdimer, and *trans*-BNdimer on the basis of their X-ray structures.

that a through-space π–π interaction can be expected. The bond length [1.476(3) Å] and angle (55.1°) between the two indole planes is appropriate for 2,2′-biindolyl.[14] Similarly, the two benzonorrole planes are close (3.46 Å) and almost parallel (5.4°) to each other in *cis*-BNdimer. A sharp contrast is observed at the 2,2′-biindolyl moiety. The bond between the two indole rings is a double bond [1.357(5) Å], which is similar to that of indigo (1.34 Å),[15] and the angle between two indole planes becomes small (10.0°). Accordingly, the difference between $BNdimerH_2$ and *cis*-BNdimer in the interactions between the two π planes could be derived not from the relative position of two benzonorrole planes but from the connection mode between the indole rings. The structural parameters for *trans*-BNdimer are similar to those of *cis*-BNdimer. Since no reduced product corresponding to *trans*-BNdimer was obtained yet, the following discussion is based on the comparison between $BNdimerH_2$ and *cis*-BNdimer (see the Supporting Information for properties of *trans*-BNdimer).[16]

Absorption spectra of $BNdimerH_2$, *cis*-BNdimer, and **9** in CH_2Cl_2 are shown in Figure 6. In the benzonorrole monomer **9**, absorption maxima are observed at $\lambda = 611$ and 645 nm, which are slightly shorter than those of the parent norrole ($\lambda = 618$ and 659 nm).[6] The absorption maximum of $BNdimerH_2$ ($\lambda = 633$ nm) is comparable to that of **9**, thus suggesting the weak interaction between two benzonorrole units in $BNdimerH_2$. Contrastingly, a remarkable red shift is observed in *cis*-BNdimer and its absorption maximum reaches up to $\lambda =$ 845 nm. Such a large red shift would indicate that the two benzonorrole π orbitals are strongly interacting with each other in *cis*-BNdimer.

Electrochemical measurements also revealed the unique electronic structure of *cis*-BNdimer. The oxidation and reduction potentials of $BNdimerH_2$, *cis*-BNdimer, and **9** in a 0.1 M Bu_4NPF_6 solution of CH_2Cl_2 are listed in Table 1. The values of E_{ox}-E_{red} (ΔE) for $BNdimerH_2$ and *cis*-BNdimer can be regarded as an approximate measure of the interaction between two benzonorrole π planes. The ΔE of **9** is 1.77 eV, which can be taken as a standard value in the case of no interaction between the two π planes. The ΔE of $BNdimerH_2$ (1.66 eV) decreased only by

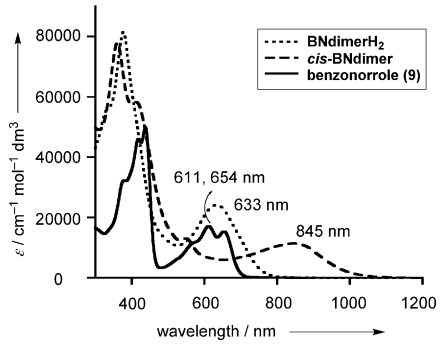


Figure 6. Absorption spectra of $BNdimerH_2$, *cis*-BNdimer, and **9** in CH_2Cl_2.

Table 1: Oxidation and reduction potentials of $BNdimerH_2$, *cis*-BNdimer, and **9**.[a]

Compound	E_{ox}	E_{red}	ΔE ($\delta\Delta E$)
$BNdimerH_2$	0.24[b]	−1.42[b]	1.66 (−0.11)
cis-BNdimer	0.47[b]	−0.98[c]	1.45 (−0.32)
9	0.31[b]	−1.46[c]	1.77 (0.00)

[a] in eV (vs. Fc/Fc^+, Pt electrode, 100 $mV s^{-1}$ scan rate).[b] Determined by differential pulse voltammetry. [c] Determined by cyclic voltammetry.

0.11 eV from that of **9**, thus suggesting weak interactions between the two π planes. Meanwhile a large decrease by 0.32 eV was observed for *cis*-BNdimer (1.45 eV), thus implying a strong interaction between the two π planes. The electrochemical properties are in good agreement with the photophysical properties.

Finally, density functional theory (DFT) calculations were performed on the model compounds of benzonorrole (**9**), $BNdimerH_2$, and *cis*-BNdimer, wherein the *meso*-C_6F_5 groups were replaced by hydrogen atoms. The Kohn–Sham orbitals are shown in Figure 7 and the orbital energies are summarized in Figure 8. For clarity, half of the structures are shown for $BNdimerH_2$ and *cis*-BNdimer in Figure 7a. Roughly speaking, the π-orbital shapes of $BNdimerH_2$ and *cis*-BNdimer are similar to those of the monomer, thus suggesting molecular orbitals of benzonorrole dimers can be constructed simply from a linear combination of those of the monomer as postulated in Figure 2. In the case of $BNdimerH_2$, both HOMO and LUMO are almost degenerate (Figure 8a). This degeneracy means that the π orbitals of the two monomer units do not interact with each other in spite of the short π–π

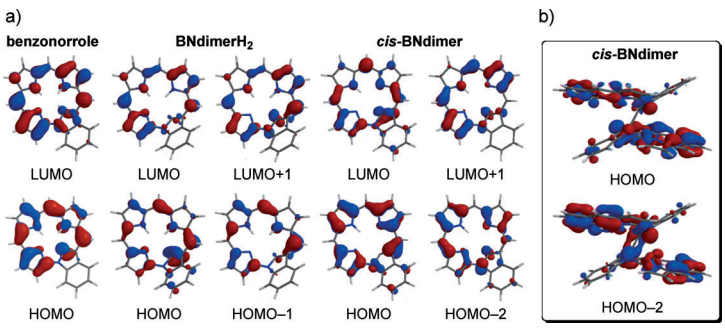


Figure 7. Molecular orbitals of a) benzonorrole, $BNdimerH_2$, and *cis*-BNdimer (top views), and b) *cis*-BNdimer (side views).

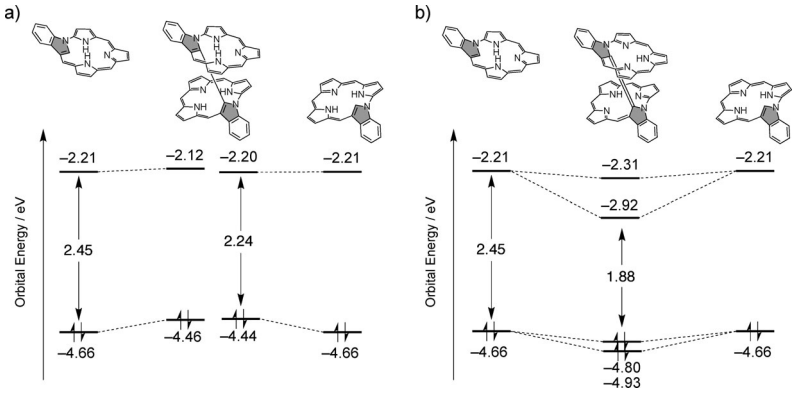


Figure 8. Interactions between the two benzonorrole π orbitals in a) $BNdimerH_2$ and b) *cis*-BNdimer.

distance (3.03 Å). A slight destabilization of HOMO and HOMO−1 could be due to the larger angle of the indole ring relative to the benzonorrole plane (56.6°). In contrast, the degeneracy of the HOMO and LUMO is completely lost in *cis*-BNdimer (Figure 8b), even with a longer π–π distance (3.36 Å). As illustrated in Figure 7b, HOMO−2 and HOMO could be regarded as an in-phase and out-of-phase combination, respectively, of the benzonorrole π orbital. As a result of the splitting of the energy level, even another orbital (HOMO−1) exists between them. The same could be said for the LUMO and LUMO+1 (see Figure S13 in the Supporting Information). Accordingly, a much narrower HOMO–LUMO gap of 1.88 eV is observed in *cis*-BNdimer, and it conforms to the experimental results. The marked contrast in the orbital interactions between $BNdimerH_2$ and *cis*-BNdimer should originate not in the π–π distance but in the bonding mode between two π planes. The difference may also affect the aromaticity of the dimers and, thus partial support for this is found in the weakening of the ring current in *cis*-BNdimer as inferred from the ^{1}H NMR chemical-shift calculations (Figure S12 in the Supporting Information).

In summary, we have synthesized benzonorrole dimers, in which two benzonorrole units are directly linked to form face-to-face π dimers with short π–π distances. Although no splitting of the orbital energy levels was observed in $BNdimerH_2$, it was clearly observed in *cis*-BNdimer. Considering similar relative positions of the two benzonorrole units, this contrast was surprising and highlights an important feature of the π–π interaction in the directly linked system. Thus, the bonding mode between the two π planes are more important than the π–π distance. Meanwhile, covalent functionalization as well as the coordination chemistry of benzonorrole would be an interesting subject, as it is the first norrole derivative that is readily available. Further studies on the benzonorrole chemistry as well as the π–π interactions in the directly linked system will be reported in the near future.

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[16] CCDC 879598 (**8**), and CCDC 879599 (**9**), CCDC 886783 (*cis*-BNdimer), CCDC 879601 (*trans*-BNdimer), and CCDC 879602 (BNdimerH2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

