Porphycenes

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meso-Dibenzoporphycene has a Large Bathochromic Shift and a Porphycene Framework with an Unusual *cis* Tautomeric Form**

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Abstract: *meso-Monobenzoporphycene (mMBPc) and meso-dibenzoporphycene (mDBPc), in which one or two benzene moieties are fused at ethylene-bridged positions (meso-positions) of porphycene, were prepared in an effort to further delocalize the π-electrons within the porphycene molecule. mMBPc and mDBPc were fully characterized by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and X-ray crystallography. The longest-wavelength Q-bands of mMBPc and mDBPc are red-shifted by 92 nm and 418 nm, respectively, compared to that of the unsubstituted porphycene (Pc). Electrochemical measurements indicate that the HOMO is destabilized and the LUMO is stabilized by the fused benzene moieties at the meso positions. Furthermore, both XPS and theoretical studies support the presence of a cis tautomeric form in the ground state of mDBPc, despite the fact that essentially all known porphycene derivatives adopt the trans tautomeric form.*

Porphycene is a constitutional isomer of porphyrin,[1] in which the symmetrically reduced porphyrinoid structure demonstrates notable physicochemical properties such as stronger absorption in the visible region[2] and tautomerization of the inner hydrogen atoms.[3] Investigation of porphycene derivatives indicate that they have potential for use as photosensitizers for photodynamic therapy[4] and as metal ligands in unique catalysts.[5] This has motivated us to prepare new porphycene derivatives with enlarged π-electron peripheries to regulate the electronic and structural features of porphycene. To this end, direct annulation of aromatic units to the porphycene framework is expected to be a useful strategy for extending the π-system, as seen in a series of benzene-fused porphyrins.[6] However, only a few reports for benzene-fused porphycene have been presented,[7] in spite of their expected unique features. Previous examples of annulated dibenzoporphycene and dinaphthoporphycene have been prepared by fusing two benzene and naphthalene moieties to the 3,4,5,6- and 13,14,15,16-positions of the porphycene framework.[8–10] In addition, tetrabenzoporphycene has four fused benzene moieties at the 2,3-, 6,7-, 12,13-, and 16,17-postions of unsubstituted porphycene (Pc) as shown in Figure 1.[11] These benzene-fused porphycenes

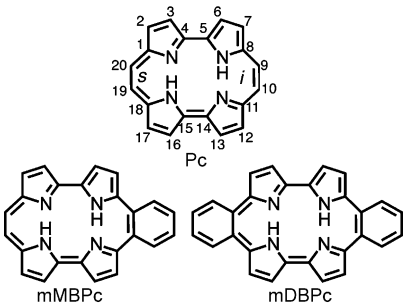

Figure 1. Molecular structures of the porphycenes in this study. The *trans* tautomeric forms are represented.

show characteristic bathochromic shifts. In efforts focused on the 9,10- and 19,20-positions (*meso* positions: *i* and *s* positions in Figure 1) of Pc as benzene fusion sites, only the monobenzene-fused derivative has been reported.[7,12] In this case, the low yield of meso-monobenzoporphycene prevents detailed evaluation of its physicochemical properties. Moreover, a dibenzene-fused *meso*-position derivative has never been prepared and has only been investigated theoretically.[13] Our research group has recently prepared benzo[*i*]porphycene (*meso*-monobenzoporphycene; mMBPc) and dibenzo[*i*,*s*]porphycene (*meso*-dibenzoporphycene; mDBPc) in good yield by using Suzuki–Miyaura coupling and intramolecular McMurry coupling reactions. In this paper, we report the preparation and characterization of the physicochemical properties of these porphycene derivatives.

The synthesis for mMBPc and mDBPc is presented in Scheme 1. Although a series of porphycene derivatives have been synthesized by the intermolecular double McMurry coupling of two 5,5′-diformyl-2,2′-biprrole molecules, mMBPc and mDBPc were obtained through intramolecular single coupling[14] of diformylated *ortho*-bis-dipyrrolylbenzene derivatives **3** and **4**, respectively. The precursor **2** was

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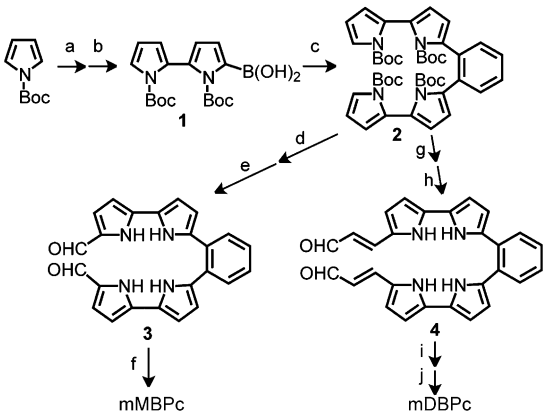

Scheme 1. Synthesis of mMBPc and mDBPc. Reaction conditions and yields: a) LTMP, $CuCl_2$, THF, 65%; b) LTMP, $B(OEt)_3$, THF, 94%; c) *o*-diiodobenzene, $[Pd(PPh_3)_4]$, K_2CO_3, H_2O/DMF, 82%; d) $POCl_3$, DMF, 93%; e) 140°C, quant.; f) Zn, CuCl, $TiCl_4$, THF, 48%; g) 180°C, ethylene glycol, 80%; h) $POCl_3$, 3-dimethylaminoacrolein, CH_2Cl_2, 97%; i) Zn, CuCl, $TiCl_4$, THF; j) *p*-chloranil, CH_2Cl_2, 20% in 2 steps. LTMP = lithium tetramethylpiperidide, THF = tetrahydrofuran, DMF = dimethylformamide.

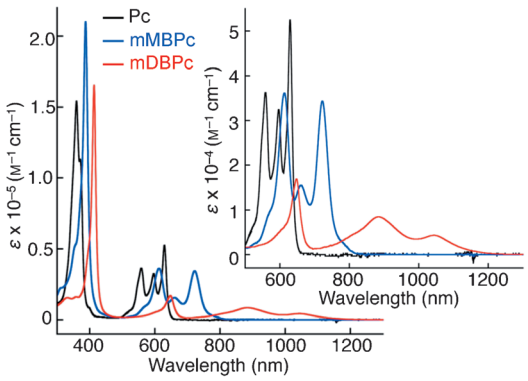

Figure 2. UV/Vis/NIR absorption spectra for Pc (black), mMBPc (blue), and mDBPc (red) in CH_2Cl_2 at 25°C. Inset: Enlarged spectra in the Q-band region.

Table 1: Comparative oxidation and reduction potentials (V) vs Ag/AgCl.[a]

	Oxidation	Reduction
Pc[b]	+1.03	−0.70
mMBPc[c]	+0.68	−0.56
mDBPc[c]	+0.41	−0.40

[a] Potential values were measured through cyclic voltammetry in CH_2Cl_2 containing 0.1 M TBAP. The ferrocene/ferrocenium redox couple (0.51 V vs Ag/AgCl) was used as a standard. [porphycene] = 1.0×10^{-3} M. [b] Scan rate: 100 mV/s. [c] Scan rate: 10 mV/s.

prepared from borylated *N*,*N*′-diBoc-2,2′-bipyrrole **1** with *o*-diiodobenzene by Suzuki–Miyaura coupling. A Vilsmeier–Haack reaction of **2** and subsequent Boc deprotection upon heating at 140°C under vacuum gave the dialdehyde **3**. The intramolecular McMurry coupling of **3** gave mMBPc in 48% yield without oxidation, although the synthesis of porphycene derivatives generally requires the oxidation of the nonaromatic intermediate after cyclization.[7] For the synthesis of mDBPc, 3-dimethylaminoacrolein was used as a reagent in the Vilsmeier–Haack reaction to yield the precursor **4**.[15] After deprotection of **2**, the acrolein moiety was introduced into each α position of the two bipyrrole units. The intramolecular McMurry coupling of **4** provided a mixture of the cyclized products. Further oxidation of the reaction mixture by using *p*-chloranil provided mDBPc in 20% yield based on **4**. Both mMBPc and mDBPc were fully characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

The UV/Vis/NIR absorption spectra of Pc, mMBPc, and mDBPc in CH_2Cl_2 are shown in Figure 2. The λ_{max} values of the Q-bands for mMBPc appear at 613, 659, and 721 nm in CH_2Cl_2. These bands are red-shifted relative to those of Pc (558, 596, and 629 nm). It is significant that the Q-band absorptions of mDBPc are located in the NIR region at 648, 884, and 1047 nm. The 418 nm deviation of the lowest-energy Q-band of mDBPc from that of Pc is much larger than those for previously reported benzene-fused porphycenes (41–135 nm).[8–11] The Soret bands of mMBPc and mDBPc are also found to be red-shifted relative to that of Pc as a result of the benzene fusion. These bathochromic shifts are generally consistent with the theoretical estimations obtained by using DFT-optimized structures (see below and Table S1 in the Supporting Information). The redox potentials of mMBPc and mDBPc were measured by cyclic voltammetry (CV) in CH_2Cl_2 (Table 1). The fused benzene moieties of the porphycene framework provide remarkably negative shifts in the oxidation reactions, while the reduction potentials are positively shifted. Considering the symmetry of the molecular orbitals, the HOMO of a butadiene unit, which is regarded as a substituent in each fused benzene moiety, interacts with the HOMO of porphycene to generate a new destabilized HOMO in both of the *meso*-benzoporphycenes (Figure 3 and Table S2 in the Supporting Information).[13] By contrast, the interaction between the LUMOs of the butadiene unit and porphycene gives a new stabilized LUMO.

The structures of mMBPc and mDBPc were determined by X-ray crystallography (Figure 4). The molecular structures in the crystals display generally planar geometries including the fused benzene moieties.[16] The bond lengths at the *meso*-

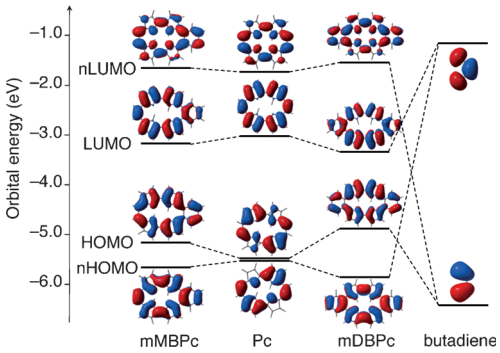

Figure 3. Molecular orbitals and of Pc, mMBPc, and mDBPc (*cis* form, see below) their energy levels. The diagram shows the interaction between Pc and butadiene units in mDBPc. Dotted lines indicate the corresponding molecular orbitals for the three porphycene molecules.

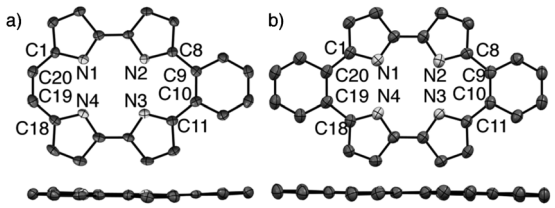

Figure 4. Crystal structures of a) mMBPc and b) mDBPc shown in ORTEP representation (thermal ellipsoids shown at 50%). Top: macrocycle plane view. Bottom: perspective view. For clarity, only selected C and N atoms are numbered and hydrogen atoms are omitted.

positions (C8–C9, C9–C10, and C10–C11 in mMBPc; C8–C9, C9–C10, C10–C11, C18–C19, C19–C20, and C20–C1 in mDBPc) are longer (> 1.43 Å) than those of Pc (< 1.40 Å)[1] and the bond lengths in each benzene moiety are clearly different (see Figure S1 in the Supporting Information), thus indicating electronic interactions between Pc and the benzene moieties. The shorter distances between the inner nitrogen atoms (N1–N4 or N2–N3) of Pc, mMBPc, and mDBPc are 2.61, 2.59, and 2.54 Å, respectively. The angles C8-C9-C10 and C9-C10-C11 in mMBPc and the angles C8-C9-C10, C9-C10-C11, C18-C19-C20, and C19-C20-C1 in mDBPc are about 129°, whereas the corresponding angles in Pc are about 132°. The shorter N1–N4 and N2–N3 distances and these angles are typical for *meso* substitution in porphycene derivatives.[12a]

The inner NH signals of mMBPc in the ^{1}H NMR spectrum ($CDCl_3$, 25 °C) appear downshifted at 7.84 ppm and 7.47 ppm, compared with that of Pc (3.15 ppm). Interestingly, the corresponding NH signal of mDBPc was observed at 8.95 ppm. The remarkable downfield shifts suggest the occurrence of stronger intramolecular NH–N hydrogen bonding.[11b,17] The results correlate with the short N1–N4 distances compared to porphycenes in the crystal structures (Figure S3 in the Supporting Information). For further evaluation of the strength of the inner NH–N hydrogen bonds, an X-ray photoelectron spectroscopic (XPS) study was carried out (Figure 5, Table 2). In the region of the N1s ionization potentials (IP), two well-resolved peaks were observed for each derivative. The peak with the highest IP value is assigned as the "protonated" nitrogen atoms and the other peak is assigned as the "unprotonated" nitrogen atoms according to the previous report.[18,19] The differences between the IP values of the protonated and unprotonated nitrogen atoms (ΔI_{N1s}) are 1.40 eV (Pc), 1.30 eV (mMBPc), and 1.15 eV (mDBPc). These values show a clear correlation with the N1–N4 distances of the compounds and are similar to

Table 2: XPS peak maxima (eV).[a,b]

	IP	Experimental ΔI_{N1s}	Calculated ΔI_{N1s} *trans* and *cis* forms
Pc	397.70, 399.10	1.40	1.38,[d] 1.46[e]
mMBPc	397.60, 398.90	1.30	1.31,[d] 1.35[e]
mDBPc[c]	397.80, 398.95	1.15	1.28,[d] 1.14[e]

[a] 180 W of monochromatized $Al_{K\alpha}$ radiation. [b] Detailed data are summarized in Table S4 in the Supporting Information. [c] The unassigned impurity at 400.0 eV was ignored. [d] *trans* form. [e] *cis* form.

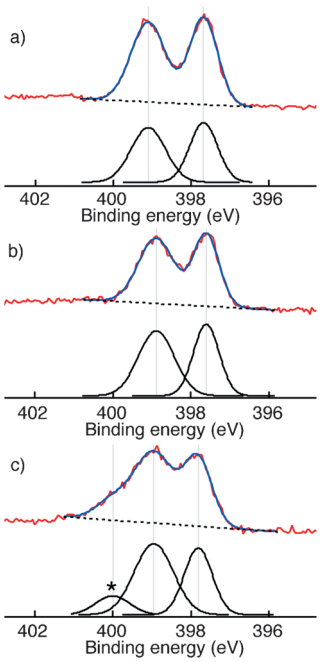

Figure 5. XPS spectra for a) Pc, b) mMBPc, and c) mDBPc. Upper spectra: raw spectra (red solid line), fitted profiles (blue solid line) and baselines (black dashed line). Lower spectra: deconvoluted profiles produced by Gaussian fitting. The peak marked with the asterisk is derived from an unassigned impurity.

the values from the previously reported data (see Figure S4 in the Supporting Information). This indicates that the smaller ΔI_{N1s} value is an indication of stronger intramolecular hydrogen bonding.[18] The IP values of *trans* and *cis* forms (Figure 6)

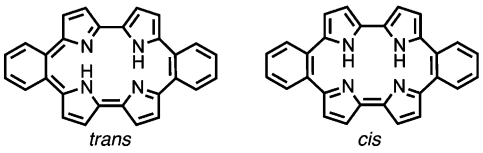

Figure 6. Possible tautomeric structures of mDBPc.

optimized by DFT calculations and the calculated ΔI_{N1s} values are shown in Table 2. In the case of mDBPc, the difference between the calculated ΔI_{N1s} values for the two tautomeric forms is relatively large (> 0.1 eV) and the experimental ΔI_{N1s} value is mostly consistent with the calculated value for the *cis* form. The present findings support the existence of the *cis* form in mDBPc.

Generally, porphycene derivatives adopt the stable *trans* form,[2,20,21] as confirmed by experimental and theoretical investigations.[22] As determined for the usual porphycene derivatives, DFT calculations indicate that the *trans* form of mMBPc is 1.6 kcal mol^{-1} more stable than the *cis* form (see Table S3 in the Supporting Information). By contrast, Waluk and co-workers reported the tautomerization of *meso*-alkylated porphycenes and demonstrated the existence of two forms (*cis* and *trans* forms) in the ground state by using supersonic jet techniques, although the *trans* form is predom-

inant according to DFT calculations.[2,3a,b,23] Interestingly, in the case of mDBPc, the DFT calculations suggests that the *cis* form is slightly more stable than the *trans* form (0.1 kcal mol^{-1} in B3LYP/6-311G**, 5.1 kcal mol^{-1} in ωB97XD/6-311G**). These theoretical data for the tautomeric forms are consistent with the XPS results.

In conclusion, mDBPc provides very unique characteristics as a result of the simple insertion of two benzene moieties at the ethylene bridges of the porphycene framework. First, the HOMO–LUMO gap is dramatically reduced as a result of electronic interaction between the fused benzene and porphycene moieties. Second, the theoretical and experimental results indicate that mDBPc exists in the *cis* tautomeric form. This is unusual for a series of porphycene derivatives. To the best of our knowledge, this is the first example of the *cis* form of porphycene being more stable than the *trans* form at the ground state. Further spectroscopic studies will contribute to the evaluation of the tautomeric form.

Keywords: extended π conjugation · NIR spectroscopy · porphycene · porphyrinoids · tautomerization

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