Diazaporphyrin Dimers

Nitrogen-Bridged Metallodiazaporphyrin Dimers: Synergistic Effects of Nitrogen Bridges and meso-Nitrogen Atoms on Structure and Properties

Masahiro Kawamata, Takuma Sugai, Mao Minoura, Yasuhisa Maruyama, Ko Furukawa, Cole Holstrom, Victor N. Nemykin, Haruyuki Nakano, and Yoshihiro Matano

Abstract: NH-bridged and pyrazine-fused metallodiazaporphyrin dimers have been prepared from nickel(II) and copper(II) complexes of 3-amino-5,15-diazaporphyrin by Pd-catalyzed C-N cross-coupling and oxidative dimerization reactions, respectively. The synergistic effects of the nitrogen bridges and meso-nitrogen atoms play major roles in enhancing the light-harvesting properties and delocalization of an electron spin over the entire \( \pi \)-skeletons of the metallodiazaporphyrin dimers.

Introduction

Covalently linked porphyrin dimers (diporphyrins) have been extensively studied not only as artificial models for the special pair in photosynthetic reaction centers but also as functional dyes for materials science.[1] It is important to understand the intrinsic effects of the spacers and linkage patterns of diporphyrin \( \pi \)-systems on their optical, electrochemical and magnetic properties because such information is indispensable for the development of porphyrin-based materials. In the last decade, several research groups have explored nitrogen-based inter-vining spacers to diversify the inherent properties of diporphyrins.[2-13] For example, Arnold and co-workers reported the first example of a diporphyrin with an NH bridge (diporphyrinylamine) P1 (Figure 1), which showed a split Soret band, indicating that excitonic coupling occurred between the two porphyrins.

Figure 1. Diporphyrinylamines P1 and P2, and pyrazine-fused diporphyrin P3.

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Ruppert and co-workers studied the effects of the intervening NH bridge on the fundamental properties of three different types of diporphyrinylamines including P1 and P2 (Figure 1)5.7 Most of these diporphyrinylamines contained two porphyrin rings that were considerably twisted at the NH bridge because of the steric repulsion between the peripheral (meso/β) substituents. As a consequence, the two porphyrin rings in P1 and P2 were not effectively conjugated. Recently, Shinokubo et al. reported the pyrazine-fused diporphyrin P3 and related compounds12,13 which showed twisted π-skeletons. Until recently, very little attention has been paid to nitrogen-bridged azaporphyrin dimers.

5,15-Diazaporphyrin (DAP) contains a π-system with intrinsic D2h symmetry, which leads to an intense electronic transition from the HOMO to the LUMO at a longer wavelength than that of porphyrin.14–16 Recently, we reported several examples of covalently linked metallo-DAP dimers (bisMDAPs) without a spacer or with an acetylene, butadiyne, or heterole spacer.17,18 The optical properties of these bisMDAPs vary considerably depending on the intervening spacer. We envisioned that nitrogen bridges could also construct highly π-conjugated bisMDAPs because (i) nitrogen is the smallest unit that allows two DAP rings to be held in close proximity, (ii) the p-orbital of nitrogen can be involved in the conjugation with the adjacent DAP π-orbital, and (iii) the NH bridge can be used as a hydrogen-bond donor towards the meso nitrogen atoms of DAP. Herein, we report the first examples of NH-bridged and pyrazine-fused bisMDAPs, as well as their precursors β-nitro- and β-amino-substituted MDAPs. The synergistic effects of the nitrogen bridges and the meso-nitrogen atoms on the structures and optical, electrochemical, and magnetic properties of the bisMDAPs are investigated.

Results and Discussion

Scheme 1 outlines the synthesis of NH-bridged and pyrazine-fused bisMDAPs. Treatment of NiDAP 1Ni with copper(II) nitrate in acetic anhydride and C6H5Cl gave 3-nitro-NiDAP 3Ni. Reduction of 2Ni with SnCl2/HCl afforded 3-amino-NiDAP 3Ni. The C–N cross-coupling reaction of 3Ni with 3-bromo-NiDAP 4Ni under standard Buchwald–Hartwig conditions (Pd(OAc)2, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (rac-BINAP), and tBuONa23) afforded NH-bridged bisNiDAP 5Ni as a black solid in 53% yield.

The pyrazine-fused bisNiDAP 6 was prepared by oxidative dimerization of 3Ni using 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (DDQ) as an oxidant based on Shinokubo’s protocol for the synthesis of P2. In contrast, treatment of 3Ni with meta-chloroperbenzoic acid (mCPBA) resulted in the oxidative reconstruction of its pyrrole ring to give diazaporpholactone 7 as the major product. This type of peripheral reconstruction from a β-aminoporphyrin was reported by Crossley in 1984.22 The NH-bridged bisCuDAP 5Cu was prepared from 1Cu according to a similar procedure to that used to synthesize 5Ni.

New compounds 2M, 3M, 5M, 6, and 7 were characterized by NMR spectroscopy, HRMS, and/or X-ray crystallography. The 1H NMR spectra of 2Ni and 3Ni in CDCl3 (Figure S1 a) exhibited singlet peaks at δ 9.30 and 7.36 ppm, respectively, which were assigned to the β2-pyrrolic protons adjacent to the nitro and amino groups, respectively. The 1H NMR spectrum of 5Ni in CDCl3 (Figure S1 b) showed only one set of DAP-derived protons (one singlet originating from the β2 proton and three sets of doublets from the other peripheral β protons), indicating that 5Ni had C2 or C2 symmetry on average. The NH proton of 5Ni (δ = 11.90 ppm) was shifted downfield compared to the NH2 proton of 3Ni (δ = 5.89 ppm) and the NH proton of P1 (δ = 6.16 ppm; in C6D6Cl2 at 100 °C). This relatively large downfield shift could be attributed not only to the ring-current effects of the neighboring DAP rings but also the intramolecular hydrogen-bonding interaction with the adjacent meso nitrogen atoms. The 1H NMR spectrum of 7 displayed three sets of doublets attributable to six β protons.

The structure of 5Ni was unambiguously elucidated by XRD analysis23. As illustrated in Figure 2, the two DAP rings and NH bridge were on the same plane with a H-N7-C3-C4 torsion angle of 3.4°, and the DAP π-planes were almost flat like that of 1Ni. From the viewpoint of molecular geometry, the two DAP π-systems in 5Ni were more effectively conjugated through the NH bridge than the two porphyrin π-systems in Arnold’s P1 where the porphyrin rings displayed a large twist angle because of steric congestion.2 The distance between the NH hydrogen and meso nitrogen (N5) atoms in 5Ni was 2.32 Å, which was considerably shorter than the sum of their van der Waals radii (2.75 Å). This implies that a hydrogen-bonding interaction between these two atoms plays a pivotal role in the formation of coplanar structure, as suggested from its
the absorption band at values of and were shifted anodically, whereas those of could be attributed to the DAP-based transitions. The TD-DFT calculations of revealed that the absorption band at for was twisted like that of Shi-nokubo’s P3; however, the twist angle between the pyrazine and pyrrole rings in was (27.0°) appreciably smaller than that of P3 (40.8°), reflecting the difference in flexibility of the NiDAP and Ni-porphyrin rings. The structure of 7 was also confirmed by X-ray crystallography (Figure S2).

The optical properties of the new DAP derivatives were studied by UV/Vis absorption spectroscopy. As shown in Figure 3a, the substitution of the proton with a nitro/amino group (from 1Ni to 2Ni/3Ni) caused substantial bathochromic shifts of the Q band of the NiDAP π-system, reflecting the electronic effects of these functional groups (see below). The absorption spectrum of NH-bridged bisNiDAP 5Ni contained multiple peaks at wavelengths longer than 500 nm. It is noteworthy that the longest-wavelength absorption bands of 5Ni (706 nm, log ε = 5.0) and 6 (647 nm, log ε = 5.1) were red-shifted and more intense than those of 2Ni (red1) and 3Ni (red2), respectively. These data imply that linking two DAP units with nitrogen is a highly promising strategy to develop new azaporphyrin-based sensitizers with broad absorption spectra reaching the near-infrared (NIR) region. The copper complexes 2Cu, 3Cu, and 5Cu exhibited similar spectral features (Figure 3c).

To gain deeper insight into the origin of the excited states of the DAP π-systems, we performed time-dependent DFT (TD-DFT) calculations on models 3Ni-m, 5Ni-m and 6-m, and magnetic circular dichroism (MCD) measurements on 3Ni and 5Ni. The results of the TD-DFT calculations qualitatively support the observed spectral features (Tables S1, S2 and Figures S4–S7). The lowest-energy excitation for each model was dominated by a HOMO-to-LUMO transition. As shown in Figures S4 and S5, the HOMOs of 3Ni-m and 5Ni-m were partially distributed on their amino groups, whereas the LUMOs were essentially localized on the DAP rings. The MCD spectra of 3Ni and 5Ni exhibited broad signals at 600–670 and 630–750 nm, respectively (Figure 3b), corresponding to the broad absorptions in the same regions. These results indicated that the HOMO-to-LUMO transitions of 3Ni and 5Ni had a substantial charge-transfer character from NH/NH (donor) to DAP (acceptor) units. Furthermore, the strong minus-to-plus MCD signals at 540–580 nm (Figure 3b), as well as the theoretically calculated results indicated that the intense absorption bands at (for 3Ni) and 561 nm (for 5Ni) could be attributed to the DAP-based π–π* transitions. The TD-DFT calculations of revealed that the absorption band at for was stemmed from DAP-based π–π* transitions.

Redox potentials of the MDAPs were measured in CH2Cl2 with Bu4NPF6 as the supporting electrolyte (Figure S8). The oxidation and reduction potentials (Eox, Ered respectively, versus ferrocene/ferrocerium) of the MDAPs are listed in Table 1. The Eox and Ered values of were shifted anodically, whereas those of 3Ni were shifted cathodically relative to the respective values of 1M. These shifts reflected typical resonance effects of the electron-withdrawing nitro group and electron-donating amino group at their periphery. The Emax and Ered values of for 5Ni (+0.41 and −1.48 V) and 6 (+0.72 and −1.25 V) were more positive than the corresponding values of 2Ni (+0.27 and −1.76 V) and 3Ni (+0.488 and −1.58 V), reflect-
Table 1. Optical and electrochemical data for DAPs measured in CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>DAP</th>
<th>$\lambda_{max}$ [nm] (log $\varepsilon$)</th>
<th>$E_{ox}$ [V]</th>
<th>$E_{red}$ [V]</th>
<th>$\Delta E$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Ni$^{ii}$</td>
<td>571 (4.8)</td>
<td>-0.80</td>
<td>-1.40, -2.02</td>
<td>2.20</td>
</tr>
<tr>
<td>1Cu$^{ii}$</td>
<td>577 (4.9)</td>
<td>+0.77</td>
<td>-1.37, -1.95</td>
<td>2.14</td>
</tr>
<tr>
<td>2Ni</td>
<td>606 (4.5)</td>
<td>+1.04</td>
<td>-1.01, -1.35, -1.93</td>
<td>2.05</td>
</tr>
<tr>
<td>2Cu</td>
<td>612 (4.5)</td>
<td>+1.01</td>
<td>-0.97, -1.29</td>
<td>1.98</td>
</tr>
<tr>
<td>3Ni</td>
<td>560 (4.2), 614 (4.1)</td>
<td>+0.40, +0.79</td>
<td>-1.50, -1.96</td>
<td>1.90</td>
</tr>
<tr>
<td>3Cu</td>
<td>574 (4.4), 619 (4.3)</td>
<td>+0.37, +0.76</td>
<td>-1.46, -1.86</td>
<td>1.83</td>
</tr>
<tr>
<td>5Ni</td>
<td>561 (4.8), 706 (5.0)</td>
<td>+0.41, +0.66</td>
<td>-1.37, -1.48, -1.93</td>
<td>1.78</td>
</tr>
<tr>
<td>5Cu</td>
<td>568 (4.7), 702 (5.0)</td>
<td>+0.40, +0.66</td>
<td>-1.33, -1.48, -1.86</td>
<td>1.73</td>
</tr>
<tr>
<td>6</td>
<td>598 (4.6), 647 (5.1)</td>
<td>+0.72, +0.96</td>
<td>-1.25, -1.42, -1.84, -1.98</td>
<td>1.97</td>
</tr>
<tr>
<td>7</td>
<td>618 (4.8)</td>
<td>+0.88</td>
<td>-1.10, -1.66</td>
<td>1.98</td>
</tr>
</tbody>
</table>

[a] Absorption maxima (> 500 nm, log $\varepsilon$ > 4). [b] Oxidation ($E_{ox}$) and reduction ($E_{red}$) potentials versus Fc/Fc$^\cdot$. The redox processes were reversible unless otherwise noted. [c] $\Delta E = E_{ox} - E_{red}$. [d] From ref. [19]. [e] Irreversible.

Conclusions

We prepared NH-bridged and pyrazine-fused bisMDAPs and investigated their structures and optical, electrochemical, and magnetic properties by X-ray crystallography, various spectroscopies, and DFT calculations. The NH-bridged bisNiDAP had a highly flat $\pi$-plane because of the presence of cooperative N–H–N(meso) hydrogen bonds. The UV/Vis absorption spectra of the new bisMDAPs displayed intense absorption bands extending to the NIR region. All the data obtained for the paramagnetic species indicated there was effective electron-spin communication between the two DAP $\pi$-systems through the nitrogen bridges. The synergistic effects of the nitrogen bridges and meso-nitrogen atoms play important roles in harvesting a wide range of visible light and delocalization of an unpaired electron spin over the entire $\pi$-skeletons of the DAPs. Further studies on the structural modification of the present DAPs aiming to provide NIR-responsive dyes are now underway.

Experimental Section

All melting points were recorded on a Y2azawa micro melting point apparatus and are uncorrected. The identity and purity of the prepared compounds were analyzed by $^1H$ (400 MHz or 700 MHz) NMR spectroscopy (Varian 400 MHz and 700 MHz spectrometers) and high-resolution mass spectrometry (Thermo Fisher Scientific EXACTIVE spectrometer; electron spray-quadrupole). The $^1H$ chemical shifts are reported in ppm as relative values versus tetramethylsilane (in CDCl$_3$ and CD$_2$Cl$_2$). The IR spectra were measured on a PerkinElmer Spectrum GX spectrometer using KBr pellets. UV/Vis absorption spectra were measured at room temperature on a JASCO V-530 or V-670 spectrometer. Electrochemical measurements (cyclic voltammetry and differential pulse voltammetry) were performed at room temperature on a CH Instruments model 650E electrochemical workstation using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ [0.01 M AgNO$_3$, 0.1 M Bu$_4$NPF$_6$ (MeCN) reference electrode. MDAP 1M$^{ii}$ and 3-bromo-MDAP 4M$^{ii}$ (M = Ni, Cu) were prepared according to their reported procedures. Other chemicals and solvents were of reagent grade quality and used without further purification unless otherwise noted. Thin-layer chromatography was performed.

Figure 4. EPR spectra of 5Cu: a) Observed in 2-MeTHF at 45 K. b) Simulated.

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formed on Kieselgel 60 F254, and preparative column chromato-
graphy was performed using Silica Gel 60, spherical, neutrality. All
reactions were performed using an argon or nitrogen atmosphere.

**Synthesis and Characterization**

2M: Copper(II) nitrate (84.3 mg, 0.35 mmol) was added to acetic
anhydride (2.0 mL), and the mixture was stirred for 10 min at room
temperature. The resulting suspension was added to a CHCl₃ solu-
tion (30 mL) of 1Ni (104.6 mg, 0.17 mmol), and the mixture was
stirred for 38 h at room temperature. The mixture was then neu-
tralized by adding an aqueous NaOH solution (10%), washed with
water, and concentrated under reduced pressure. The residue was
subjected to column chromatography on silica gel (hexane/AcOEt = 10:1). Compound 2Ni (Rf = 0.44) was isolated as a dark
purple solid (98.0 mg, 89%) by recrystallization from CH₂Cl₂/MeOH.
According to a similar procedure, 2Cu (Rf = 0.24; hexane/AcOEt =
10:1) was prepared in 57% yield from 1Cu. 2Ni: m.p. > 300 °C;
1H NMR (700 MHz, CDCl₃): δ = 1.81 (s, 12H, ortho-Me), 2.60 (s, 3H,
para-Me), 2.62 (s, 3H, para-Me), 7.27 (s, 2H, meta-H), 7.28 (s, 2H,
meta-H), 8.74 (d, J = 4.9 Hz, 1H, pyrrole-β), 8.76 (d, J = 4.9 Hz, 1H,
pyrrole-β), 8.77 (d, J = 4.9 Hz, 1H, pyrrole-β), 9.08 (d, J = 4.9 Hz, 1H,
pyrrole-β), 9.13 (d, J = 4.9 Hz, 1H, pyrrole-β), 9.26 (d, J = 4.9 Hz,
1H, pyrrole-β), 9.30 ppm (s, 1H, pyrrole-H); UV/Vis (CHCl₃): λ_max
(ε) = 368 (44000), 407 (53500), 606 (65 nm (3000 m⁻¹ cm⁻¹); HRMS (ESI): m/z calcd for C₃₇H₄₂N₁₀O₇: 655.1800; found: 655.1732 [M+H⁺]. 1Cu:
m.p. > 300 °C; UV/Vis (CHCl₃): λ_max (ε) = 380 (41000), 415 (52000),
612 nm (31000 m⁻¹ cm⁻¹); HRMS (ESI): m/z calcd for C₃₇H₄₂N₁₀O₇:
655.1752; found: 655.1734 [M+H⁺].

3M: A mixture of 2Ni (40.5 mg, 0.062 mmol), SnCl₄·2H₂O (75.2 mg,
0.33 mmol), 3 mL HCl (1 mL), and CH₂Cl₂ (25 mL) was heated under
reflux conditions for 0.5 h. The mixture was then neutralized by
adding an aqueous NaOH solution (10%), washed with water, and
concentrated under reduced pressure. The residue was subjected
to column chromatography on silica gel (hexane/AcOEt = 7:1).
Compound 3Ni (Rf = 0.41; hexane/AcOEt = 5:1) was isolated as
a purple solid (31.3 mg, 82%) by recrystallization from CHCl₃/MeOH.
According to a similar procedure, 3Cu (Rf = 0.52; hexane/AcOEt =
5:1) was prepared in 57% yield from 2Cu. 3Ni: m.p. > 300 °C;
1H NMR (700 MHz, CDCl₃): δ = 1.80 (s, 6H, ortho-Me), 1.82 (s,
1H, ortho-Me), 2.59 (s, 3H, para-Me), 2.60 (s, 3H, para-Me), 5.82
(s, 2H, NH₂), 7.24 (s, 2H, meta-H), 7.25 (s, 2H, meta-H), 7.36 (s, 1H,
pyrrole-β), 8.64 (d, J = 4.3 Hz, 1H, pyrrole-β), 8.70 (d, J = 4.3 Hz,
2H, pyrrole-β), 8.79 (d, J = 4.3 Hz, 1H, pyrrole-β), 9.03 (d, J = 4.3 Hz,
1H, pyrrole-β), 9.05 ppm (d, J = 4.3 Hz, 1H, pyrrole-β); λ_max
(ε) = 387 (64000), 560 (16000), 614 nm (12000 m⁻¹ cm⁻¹); HRMS (ESI): m/z calcd for C₃₇H₄₂N₁₀O₇: 620.2067; found: 620.2061 [M+H⁺]. 3Cu: m.p.
> 300 °C; UV/Vis (CHCl₃): λ_max (ε) = 373 (68000), 390 (70000), 574
(23000), 616 nm (19000 m⁻¹ cm⁻¹); HRMS (ESI): m/z calcd for
C₃₇H₄₂N₁₀O₇: 625.2010; found: 625.1990 [M+H⁺].

5M: A mixture of 3Ni (18.4 mg, 0.030 mmol), 4Ni (16.6 mg,
0.024 mmol), Pd(OAc)₂ (1.6 mg, 0.006 mmol), tBuO-Na (3.5 mg,
0.072 mmol) and toluene (10 mL) was heated under reflux condi-
tions for 6 h. After being cooled, the mixture was washed with water and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/AcOEt = 10:1). Compound 5Ni (Rf = 0.41; hexane/AcOEt = 5:1) was isolated as a black solid (15.7 mg, 53%) by recrystallization from CH₂Cl₂/MeOH. According to a similar pro-
cEDURE, 5Cu (Rf = 0.42; hexane/AcOEt = 5:1) was prepared in 36% yield from 3Cu.

Selected X-ray Crystallographic Data

5Ni: Molecular formula = C₃₇H₄₂N₁₀O₇, molecular weight = 1921.09, 0.20×0.10×0.05 mm, orthorhombic, Pnam, a = 18.9570(9) Å, b = 38.5630(18) Å, c = 11.9954(6) Å, V = 8416.9(7) Å³,
Z = 4, μ_cad = 1.516 cm⁻¹, μ = 10.10 cm⁻¹, collected 75905, inde-
pendent 9798, parameters 585, R₁ = 0.1173 (all data), R1 = 0.0477
(I > 2σ(I)), GOF = 1.102. CCDC 1528879.

The crystallographic data for 6 and 7 could not be fully refined to
a satisfactory level because of uncertain loss of solvent molecules
included in the crystal (for 6) or positional disorder (for 7). Regard-
ing the positional disorder of 7, the lactone part was located in
each pyrrole ring crystallographically, with occupancies of the OCO
unit of 0.2, 0.3, 0.2 and 0.3 at the rings.

**DFT Calculations**

The geometries of 3Ni-m, 5Ni-m, 6-m, and 5Ni-m⁺ were opti-
mized using the DFT method in which the solvent effect of CH₂Cl₂
was included by the polarizable continuum model (PCM). The basis
sets used were 6-31G(d,p) basis set (20) for H, C, and N and the
Wachters–Hay all-electron basis set (21) supplemented with one
The Cartesian coordinates are summarized in Table S1. The excitation energies and oscillator strengths listed in Table S2 were computed using the TD-DFT method. All of the calculations were carried out using the Gaussian 09 suite of programs. Selected Kohn–Sham orbitals and their energies are summarized in Figures S4–S6.

EPR Measurements
5Ni+: A solution sample of 5Ni (1 m) and Bu₄NPF₆ (0.1 m) in CH₂Cl₂ in an electrolysis EPR cell with two electrodes was prepared. The electrolysis EPR spectra were recorded using a JEOL JES-FA200 spectrometer under a 3.6 V Matusada Precision PL-18-5 current source at room temperature. Spectral simulation was performed using EasySpin,[26] a MATLAB toolbox. The selected spin-Hamiltonian parameters are summarized in Figure S10.

5Cu: A solution sample of 5Cu in 2-methyltetrahydrofuran in a quartz EPR tube was degassed by repeated freeze/pump/thaw cycles and sealed under the vacuum by flame. The continuous-wave (cw) EPR spectra for 5Cu were recorded using a JEOL JES-FA200 spectrometer equipped with an OXFORD ESR900 He-flow-type cryostat. The measurement temperature was controlled by an OXFORD Mercury temperature controller. The selected spin-Hamiltonian parameters are summarized in Figure S11.

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Keywords: diazaporphyrins • EPR spectroscopy • macrocycles • porphyrins • transition metals

[23] CCDC 1528879 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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