CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800517

Porphyrin Dimers Bridged by an Electrochemically Switchable Unit

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Dedicated to Professor Chi-Kwong Chang on the occasion of his 60th birthday

In the past decade much effort has been devoted to the synthesis and studies of molecular systems comprising porphyrin units bridged by well-defined π-conjugated spacers at the *meso*- or β-positions.[1–4] These conjugated oligoporphyrin systems are expected to have potential applications in molecular wires and electronic devices due to their unique optical, physical, and chemical properties. Photophysical studies on electron transfer of a series of ferrocene–oligoporphyrin–fullerene triads show that a *meso–meso* butadiyne-bridged oligoporphyrin acts as an efficient molecular wire for long-range charge transfer over 65 Å.[5] More recently, the conductivity measurements on butadiyne-bridged porphyrin polymers indicate that the formation of double-strand 4,4′-bipyridyl ladder complex by addition of bipyridine to the single-strand porphyrin polymer leads to an increase in conductivity by an order of magnitude.[6] EPR studies performed by Therien and co-workers on *meso–meso* ethyne-linked porphyrin oligomers show that this type of conjugated molecules is able to mediate charge migration over a distance of about 75 Å.[7] The synthesis of *meso–meso*, β–β, β–β triply-linked porphyrin tapes reported by Osuka represents a milestone in the area of porphyrin molecular wires.[3] The fully conjugated porphyrin tapes exhibit remarkable properties including very low optical HOMO–LUMO gap, low oxidation potential and rigid structure, and they may find use in a variety of molecular electronics.

Despite extensive studies on the conjugated porphyrin arrays, oligoporphyrin molecular wires that show switchable conductance states by chemical or electrochemical means are rare. One example is the porphyrin arrays in which the individual macrocyles are laterally-linked by a quinonoid unit at the β,β'-positions of the porphyrin rings.[8] In this system, the electronic communication between porphyrin units can be modulated by quinonoid/benzenoid conversion using chemical or electrochemical means. Another example of switchable porphyrin wires is the systems where proquinoidal units bridge two porphyrins.[9] It is well known that the reversible conversion between quinone and hydroquinone can be achieved by chemical or electrochemical methods.[10] Incorporation of a quinone unit into the central part of a porphyrin dimer via acetylene linkers would allow the interporphyrin interaction to be switched off and on in a controllable fashion and this type of molecules may have the potential for the application in switchable molecular wires. Therefore, we set out to design and synthesize a series of porphyrin dimers Ni_2**2**, Ni_2**3**, and Ni_2**4** to explore their potential as redox-controllable switching molecules.

The synthetic routes to porphyrin dimers Ni_2**2**, Ni_2**3**, and Ni_2**4** were outlined in Scheme 1.[11] The coupling reaction of porphyrin Ni**1** with the diiodide gave porphyrin dimer Ni_2**2**.[12] Demethylation of Ni_2**2** to give Ni_2**3** employing excess BBr_3 was unsuccessful. However, the demethylation can be achieved by the reaction of excess BBr_3 with the free base of the zinc analogue Zn_2**2**, obtained by a procedure similar to that for Ni_2**2**.[13] Subsequent nickel insertion afforded porphyrin dimer Ni_2**3**. The oxidation reaction of dimer Ni_2**3** with PbO_2 gave porphyrin Ni_2**4**.[14] For comparison purposes, porphyrin Ni**5** was synthesized by employing a procedure similar to that for Ni_2**2**. The molecular structures of these porphyrins were confirmed by various spectroscopic methods such as NMR, UV/Vis, IR spectroscopy, and mass spectrometry.

Figure 1 shows the crystal structure of compound Ni**5**.[15] The bond lengths and angles fall in the normal range. The porphyrin ring adopts an essentially planar conformation

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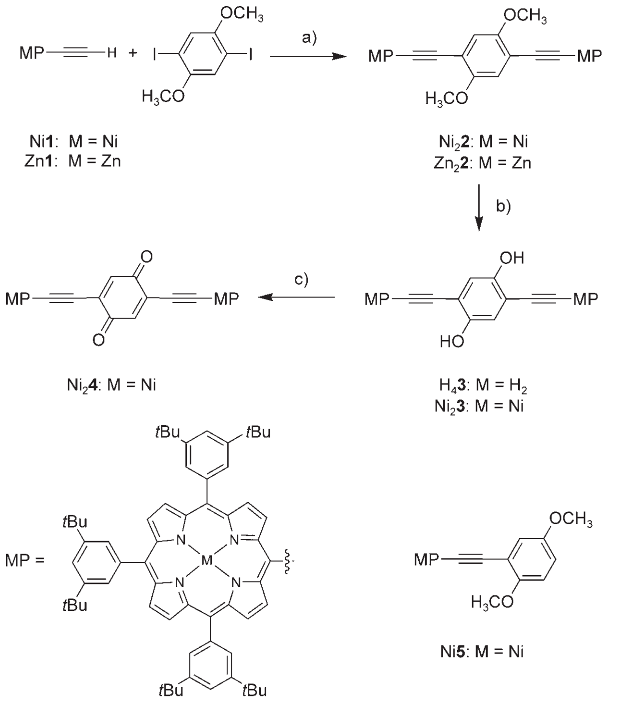


Scheme 1. Synthesis of porphyrin dimers. a) $AsPh_3$, $[Pd_2(dba)_3]$, NEt_3 (Ni_2**2**, 82 %; Zn_2**2**, 89 %). b) i) Zn_2**2**, 20 % HCl, CH_2Cl_2; ii) BBr_3, CH_2Cl_2; iii) $Ni(OAc)_2{\cdot}4H_2O$, $CHCl_3$/AcOH (Ni_2**3**, 43 % over 3 steps); c) PbO_2, CH_2Cl_2 (90 %).

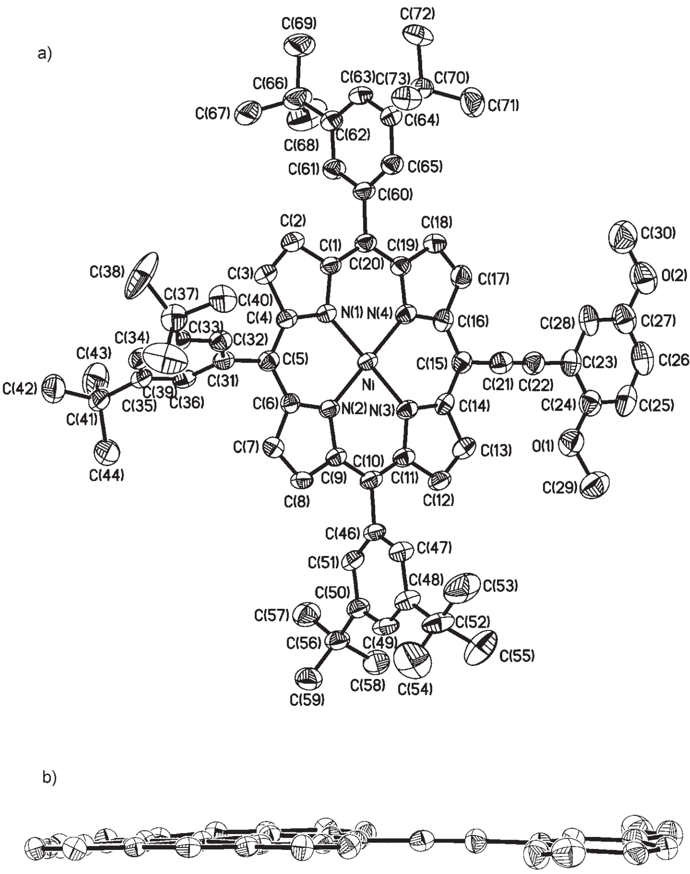


Figure 1. X-ray crystal structure of Ni**5**. a) Top view. b) Side view (*meso*-substituted aryl groups omitted for clarity). The thermal ellipsoids were drawn at the 50 % probability level.

and is nearly coplanar with the dimethoxyphenyl ring. The coplanar arrangement can be ascribed to the crystal packing forces.[11,16] It is possible that the two porphyrin rings and the bridge in dimers Ni_2**2** and Ni_2**3** are coplanar in the solid-state. The rigid and conjugated spacers in Ni_2**2** and Ni_2**3** would facilitate the electronic coupling between the porphyrin units although the spacers can undergo free rotation in solution.

The absorption spectra of porphyrin dimers Ni_2**2**, Ni_2**3**, and Ni_2**4** and reference compound Ni**5** in THF are summarized in Figure 2 and Table 1. The spectrum of dimer Ni_2**2** displays a quite similar feature to that of Ni_2**3**, suggesting that the dimethoxybenzene and hydroquinone units in Ni_2**2** and Ni_2**3**, respectively, mediate the interporphyrin interaction in a similar way. As compared to that of Ni_2**4**, the Soret bands of Ni_2**2** and Ni_2**3** show peak-broadening and red-shift. The full width at half maximum (FWHM) is calculated to be 4386 cm^{-1} for Ni_2**3**, which is much larger than that for Ni_2**4** (FWHM = 2098 cm^{-1}). It should be noted that Ni_2**4** shows a broad band at 15 965 cm^{-1} in THF, which shifts to 15 210 cm^{-1} in a mixture of $CHCl_3$/MeOH (2:1), while the Soret and Q(1,0) bands are only slightly shifted (Figure S1 in the Supporting Information). Most likely this broad band consists of both the Q(0,0) band and charge transfer band from the porphyrin to the quinone unit. Further studies on the nature of this broad band will be continued. Comparison of the Soret band for porphyrin Ni_2**2** with that for reference compound Ni**5** confirms that peak-broadening of Ni_2**2** is not induced by the electronic interaction between the porphyrin and dimethoxylphenyl units. A significant increase in the intensity of Q bands for Ni_2**2** and Ni_2**3** relative to that for Ni**5** was observed. These spectral features for Ni_2**2** and Ni_2**3** can be explained by a decrease of the energy gap between HOMO and LUMO as a result of the extended π-conjugation and indicate that there is strong interporphyrin interaction mediated by the benzenoid unit.[17] In the case of Ni_2**4**, the quinone bridge containing isolated double and single bonds effectively disrupt the electronic coupling between the two porphyrin ends.

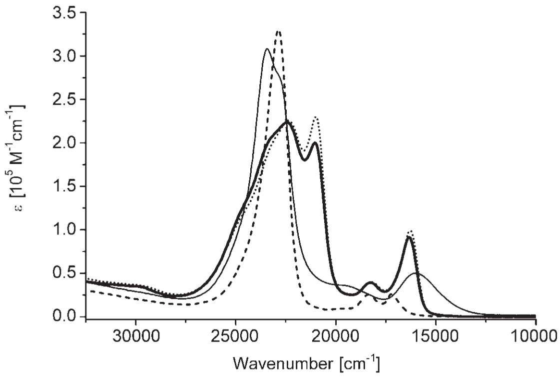


Figure 2. Absorption spectra of Ni_2**2** (•••••), Ni_2**3** (——), Ni_2**4** (——), and Ni**5** (-----) in THF.

Table 1. Absorption data for porphyrins Ni$_2$**2**, Ni$_2$**3**, Ni$_2$**4**, and Ni**5**.

	λ_B [cm^{-1}] (logε)[a]	λ_Q [cm^{-1}] (logε)[a]	FWHM[b]	Absorption λ [cm^{-1}][c]	Absorption λ [cm^{-1}][c]
	Neutral form		B-band [cm^{-1}]	Mono-cation	Di-cation
Ni$_2$**2**	22371 (5.35), 21008 (5.36)	18215 (4.60), 16287 (4.99)	4262	23529, 16666, 12345, 3385	24390, 20408, 13888, 7576
Ni$_2$**3**	22371 (5.35), 21008 (5.30)	18248 (4.60), 16313 (4.96)	4386		
Ni$_2$**4**	23365 (5.48)	19305 (4.52), 16026 (4.71)	2098		
Ni**5**	22831 (5.52)	18315 (4.41), 17212 (4.41)	1380		

[a] The absorption spectra was taken in THF. [b] FWHM is the full width at half-maximum height. [c] The oxidized species of Ni$_2$**4** and Ni**5** are relatively unstable.

A simple way to evaluate intramolecular interaction between the porphyrin units in porphyrin arrays is to study their electrochemical properties. It is anticipated that two one-electron oxidations for the first electron abstraction from the porphyrin units of Ni$_2$**3** should be observed if the individual macrocycles are electrochemically coupled. However, the electrochemical reactions of dimer Ni$_2$**2** instead of Ni$_2$**3** were studied since the oxidation of the hydroquinone bridge in Ni$_2$**3** occurs prior to that of the porphyrin rings and the 1,4-diethynyl-2,5-hydroxyphenyl and 1,4-diethynyl-2,5-dimethoxyphenyl bridges in Ni$_2$**2** and Ni$_2$**3**, respectively, should modulate the interporphyrin interaction in a similar way as evinced by the absorption spectra. The electrochemistry of Ni$_2$**2** and Ni$_2$**4** were investigated by cyclic voltammetry and differential pulse voltammetry. As shown in Figure 3, porphyrin dimer Ni$_2$**2** exhibits two overlapping one-electron reversible oxidations at potentials of $E_{1/2}$(ox1) = +0.90 and $E_{1/2}$(ox2) = +0.99 V, which are resolved by using differential pulse voltammetry, and a two-electron process at $E_{1/2}$(ox3) = +1.27 V. The first two one-electron oxidation processes can be assigned to successive formation of the monocation and dication, indicative of strong interporphyrin interaction in Ni$_2$**2**. The separation of the redox potentials $E_{1/2}$(ox1) and $E_{1/2}$(ox2) is 90 mV and the comproportionation constant (K_c) was estimated to be 22.[18] As compared to the 1,4-ethynylphenyl-bridged nickel porphyrin dimer,[19] in which the first two one-electron oxidation potentials in CH_2Cl_2 at 298 K are separated by 50 mV, our porphyrin Ni$_2$**2** shows a stronger electronic coupling between the porphyrin units via the bridge. This may be ascribed to the better energy proximity of the frontier orbitals of the porphyrin units and those of the 1,4-diethynyl-2,5-dimethoxyphenyl linker because the electron-donating nature of the methoxyl groups would elevate the energy of both HOMO and LUMO of the linker. The cyclic voltammogram of Ni$_2$**4** (Figure 3) shows that the first two-electron oxidation occurs at $E_{1/2}$ = +1.08 V corresponding to the first electron abstraction from both the porphyrin rings to form Ni$_2$**4**$^{2+}$, indicating that the two porphyrin units do not show electronic coupling via the quinone bridge. The second two-electron oxidation corresponding to the formation of Ni$_2$**4**$^{4+}$ was observed at $E_{1/2}$ = +1.27 V. In the reduction region, the first two one-electron processes at $E_{1/2}$ = −0.26 and E_{pc} = −0.72 V can be assigned to the reductions of the quinone unit and the two-electron process at a potential of −1.37 V corresponds to the first electron addition to both the porphyrin rings.

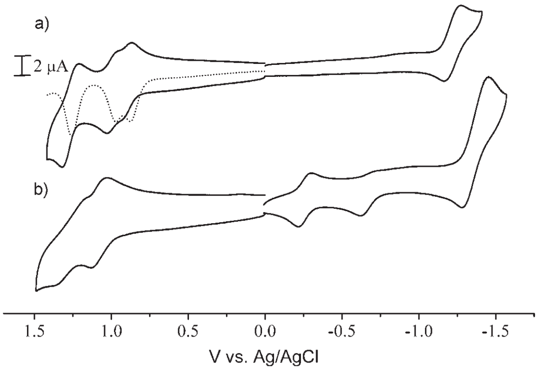


Figure 3. a) Cyclic voltammograms (——) and differential pulse voltammograms (•••••) for Ni$_2$**2** and b) cyclic voltammograms for Ni$_2$**4** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at a scan rate of 0.1 V s^{-1}.

Calculations of molecular orbitals of Ni$_2$**2** were performed by the PM3 method using Spartan ′06 (Figure S2 in the Supporting Information). The building blocks used for the construction of Ni$_2$**2** were taken from the crystal structure of porphyrin Ni**5**, the symmetry of the molecule was unconstrained to C_1. For Ni$_2$**2**, the electron density is significantly distributed to the π-system of both porphyrin rings and the bridge at the HOMO and LUMO, suggesting significant interaction between the two porphyrin rings, that is, the porphyrin units would behave as electrochemically dependent groups. In the case of the quinone-bridge dimer Ni$_2$**4**, the electron density of the HOMO is essentially localized on the two porphyrin rings and the LUMO is mainly contributed from the diethynylquionone unit. Furthermore, slight splitting (0.1 eV) of HOMO and HOMO-1 for Ni$_2$**2**, which was absent in Ni$_2$**4**, was observed. These results are in a good agreement with the absorption spectra and electrochemical measurements.

To gain insight into the interporphyrin interaction in dimer Ni$_2$**2**, the oxidations were further investigated by electronic absorption. Figure 4 shows the UV/Vis-near IR spectra of Ni$_2$**2**, Ni$_2$**2**$^{+}$, and Ni$_2$**2**$^{2+}$. The monocation Ni$_2$**2**$^{+}$ was generated in situ by reacting Ni$_2$**2** with one equivalent of $[(p\text{-}BrC_6H_4)_3N][SbCl_6]$ in CH_2Cl_2. The corresponding dication Ni$_2$**2**$^{2+}$ can be generated by further addition of another equivalent of $[(p\text{-}BrC_6H_4)_3N][SbCl_6]$. Both monocation Ni$_2$**2**$^{+}$ and dication Ni$_2$**2**$^{2+}$ are relatively stable since they can be converted back to the neutral form of compound Ni$_2$**2** by reacting with a slight excess of ferrocene. In the near-IR region, the monocation Ni$_2$**2**$^{+}$ displays a broad intervalence charge transfer (IVCT) band near the detection limit of 3385 cm^{-1}, which disappears upon further oxidation to the corresponding dication $Ni_2\mathbf{2}^{2+}$. In this porphyrin dimer system, the existence of the IVCT band upon one-electron oxidation again demonstrates strong electronic coupling between the two porphyrin units. For comparison purposes, $Ni_2\mathbf{4}$ and $Ni\mathbf{5}$ were oxidized under similar conditions and a broad IVCT band was not observed for the oxidized species (Figures S3 and S4 in the Supporting Information).

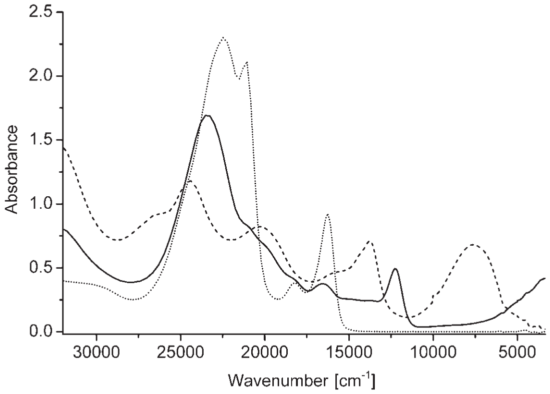
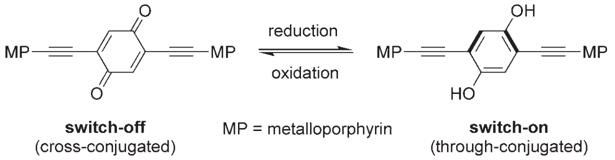


Figure 4. UV/Vis-NIR spectra of porphyrin dimer $Ni_2\mathbf{2}$ (••••), monocation $Ni_2\mathbf{2}^{+}$ (——), dication $Ni_2\mathbf{2}^{2+}$ (-----).

We proposed a simple synthetic approach that allows us to incorporate a redox-active bridge into a porphyrin dimer. In comparison with those of dimer $Ni_2\mathbf{4}$, the electronic absorptions of porphyrin dimers $Ni_2\mathbf{2}$ and $Ni_2\mathbf{3}$ exhibit significant peak-broadening and red shifts. The redox potentials of the first and second oxidations for $Ni_2\mathbf{2}$, corresponding to the formation of $Ni_2\mathbf{2}^{+}$ and $Ni_2\mathbf{2}^{2+}$ species, are separated by 90 mV. The mixed-valence species $Ni_2\mathbf{2}^{+}$ shows a broad IVCT band and this broad IVCT band disappears for $Ni_2\mathbf{2}^{2+}$ species. These spectroscopic and electrochemical data confirm that the two porphyrin units in $Ni_2\mathbf{2}$ and $Ni_2\mathbf{3}$ exhibit strong electronic coupling while those in $Ni_2\mathbf{4}$ are essentially independent. Thus, we propose that in dimer $Ni_2\mathbf{4}$ the quinone bridge can be reversibly switched off and on by electrochemical or chemical means from cross-conjugated quinonoid to through-conjugated benzenoid states (Scheme 2). This type of porphyrin dimers holds promise to be used in the application of controllable molecular switches. Further studies on the switching properties of these porphyrin arrays and related analogues are underway in our laboratory.



Scheme 2. Redox-controlled molecular switches.

Acknowledgements

The authors acknowledge the National Science Council of Taiwan for financial support. This work is supported in part by the Ministry of Education of Taiwan, under the ATU plan.

Keywords: conjugation · cross-coupling · electrochemistry · molecular electronics · porphyrinoids

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of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: March 20, 2008