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Dimensionally Oriented Redox-active π-Conjugated Systems

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Summary: Porphyrins bearing the redox-active phenylenediamine pendant groups are synthesized to afford dimensionally oriented π-conjugated systems. The structural and electronic characteristics depend on the atropisomers. In the fluorescence emission spectra, the emission from the porphyrin moiety is almost completely quenched. Zinc complexation of the αααα isomers gives the corresponding zinc porphyrins bearing four phenylenediamine strands. Treatment with a bidentate ligand, DABCO, leads to the sandwich dimer complex, in which the porphyrin moieties are surrounded by π-conjugated pendant groups. *p*-*t*-Butylcalix[4]arenes bearing four redox-active phenylenediamine pendant groups on the lower rim are synthesized and characterized both spectroscopically and electrochemically. The interconversion of the oxidation states of the pendant groups is demonstrated both chemically and electrochemically.

Keywords: calixarene; conjugated polymer; dimensional control; porphyrin; redox-active system; redox polymer

Introduction

Architecturally ordered orientation of π-conjugated molecular or polymer chains is expected to construct novel π-electronic systems. Only few reports have appeared on the alignment of π-conjugated polymer or telomer chains.[1] Dimensional orientation of π-conjugated molecular chains in one molecule is envisioned to provide such a system. In this context, the utilization of a cyclic scaffold is considered to be a convenient approach to orient the π-conjugated molecular chains. This review describes the porphyrins and calix[4]arene bearing the phenylenediamine pendant groups, which are directed towards the construction of dimensionally oriented redox-active π-conjugated systems.

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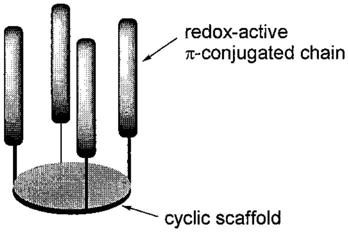


Fig. 1. Orientation of redox-active π-conjugated systems.

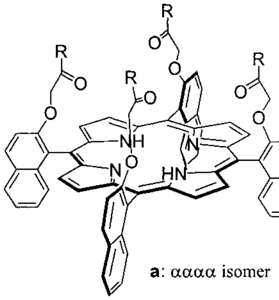
Porphyrins Bearing Four Phenylenediamine Pendant Groups

A number of porphyrin–chromophore hybrid systems have been synthesized since porphyrins are photochemically active. Electronic communication and/or photoinduced electron and energy transfer between the porphyrin and chromophore centers are achieved in these systems.[2] Chromophores are introduced along or onto the porphyrin plane to give two-dimensionally[3] or face-to-face[4] arrayed electronic systems, respectively. The latter interaction has been reported in strapped porphyrins[4a-e] and other linked porphyrins.[4f-j] π-Conjugated oligomer chains such as oligothiophene[5] and oligophenylene[6] have been also introduced to the porphyrin ring to form two-dimensional π-electronic systems, in which π-conjugated oligomers are incorporated along the porphyrin plane. *meso*-Tetraarylporphyrin, in which four aromatic rings at the *meso*-position are perpendicular to the porphyrin plane, can be used for perpendicular alignment of π-conjugated chains on the porphyrin plane. Furthermore, atropisomerism of *meso*-tetraarylporphyrins has an advantage of aligning π-conjugated pendant groups under the controlled orientation. Such an alignment is considered to permit unique electronic communication among the π-conjugated pendant groups or between the pendant group and porphyrin ring although the expanded π-conjugation is disrupted. The porphyrins bearing the redox-active phenylenediamine pendant groups are herein designed from these points of view.[7,8]

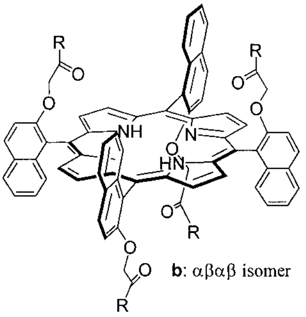
The porphyrins **4-5** are synthesized by introduction of four phenylenediamine pendant groups into the porphyrin scaffold **1** without atropisomerization as shown in Scheme 1. The structure of these porphyrins is elucidated by NMR. A higher shift is observed with the phenylene protons of the strands due to the ring-current effect of the porphyrin π-ring system. Furthermore, the strands of **4b** and **5b** are more susceptible to the effect than **4a** and **5a**.

$$\mathbf{1a}\ (\mathbf{1b}) \xrightarrow{\substack{1)\ 1\ \mathrm{N\ NaOHaq} \\ 2)\ \mathrm{CH_3COOH}}} \mathbf{2a}\ (\mathbf{2b}) \xrightarrow{\substack{1)\ 1,1'\text{-carbonyldiimidazole} \\ 2)\ \mathbf{3}}} \mathbf{4a}\ \text{or}\ \mathbf{4b}$$

Scheme 1.



a: αααα isomer

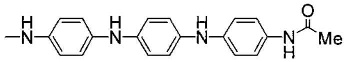


b: αβαβ isomer

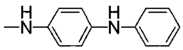
1: R = —OEt

2: R = —OH

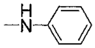
4: R =



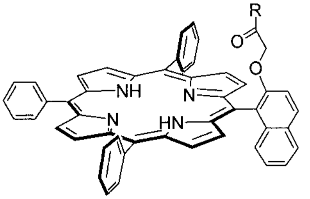
5: R =



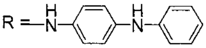
6: R =



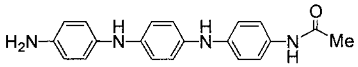
7: R = —NHPr



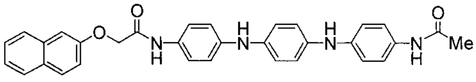
8: R =



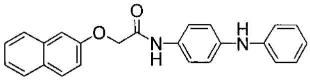
3:



9:



10:



The electronic environment of these porphyrins is also investigated by absorption spectra. The slightly red-shifted Soret band with the lower molar coefficient is observed in both cases of **4a** and **4b** in THF, as compared with the propyl-substituted derivatives **7a** and **7b**. The Soret and Q bands of **4b** are more broadened than those of **4a**, being in contrast to the lack of typical spectral difference between the atropisomers 7. These bands of **5** in dichloroethane are also red-shifted and broadened as observed in **4**.

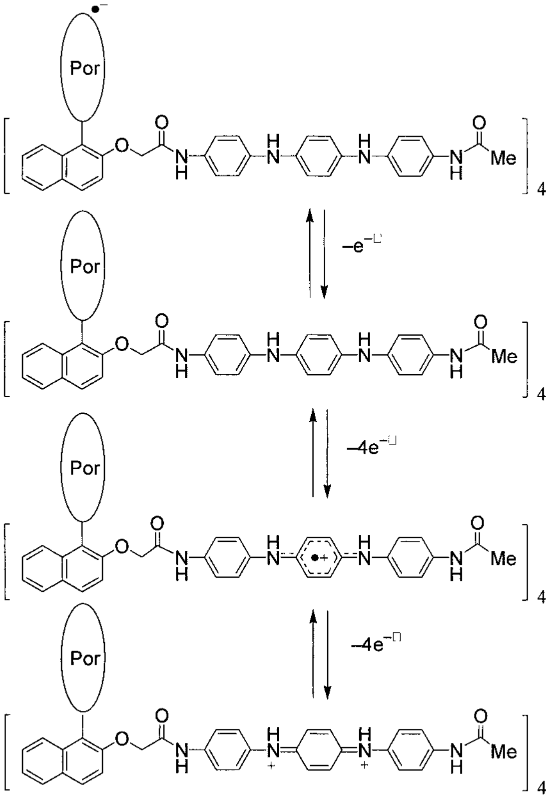
The spectral difference between the αααα and αβαβ isomers might be accounted for as follows. The pendant groups of the αβαβ isomer might be in equilibrium with the conformers, in which one or more strands lean toward the porphyrin ring. The equilibrium of the conformers is assumed to be related to the distortion and fluctuation of the porphyrin ring as indicated by the broadened Soret and Q bands. On the other hand, such a conformation is less accessible in the αααα isomer probably due to the steric crowdedness, being accompanied by the restricted motion of the phenylene moieties of the pendant groups. Molecular dynamics calculation also supports these conformations.

The pendant group of the porphyrin **8**, which bears one anilinoanilino pendant group, is also susceptible to the ring-current effect as observed in the αβαβ isomer **5b**. The single-crystal X-ray structure analysis demonstrated that the pendant group of **8** leans toward the porphyrin ring. These results support the above-mentioned conformation of **5b**, in which the pendant groups and porphyrin ring are present in close proximity.

The redox processes attributable to the phenylenediamine and porphyrin moieties are illustrated in Scheme 2. Although the oxidation potentials of the phenylenediamine moieties of **4a** and **4b** are not largely different, they are more cathodic than those of **9**. A similar trend is observed with **5a** and **10**. This shift might be based on the characteristics of the present π-conjugated system, which suggests an electronic interaction between the pendant groups on the porphyrin scaffold.

The fluorescence emission spectroscopy with excitation of the Q(1,0) band is studied. The porphyrin moiety observed in **7** is almost completely quenched (< 1%) in the case of **4a** and **4b**. Contrary to **4**, a similar quenching does not occur with **6** bearing the anilino pendant groups. Quenching of the emission of **4** is likely to depend on the phenylenediamine function of the pendant group. This process is consistent with the difference in the redox potentials of each unit.

In the case of **4a**, the photoinduced intramolecular electron transfer from the phenylenediamine moiety to the excited singlet state of the porphyrin is thermodynamically feasible. The quenching behavior of **4b** is explained similarly. The emission of **5a** or **5b** is quenched as observed in **4** (ca. 1%). On the contrary, **8** exhibits the emission with ca. 50% intensity as compared with that of **7**. The difference observed between **5** and **8** might be reflected by the π-conjugated strand system of **5**, in which the pendant groups undergo the more facile oxidation.



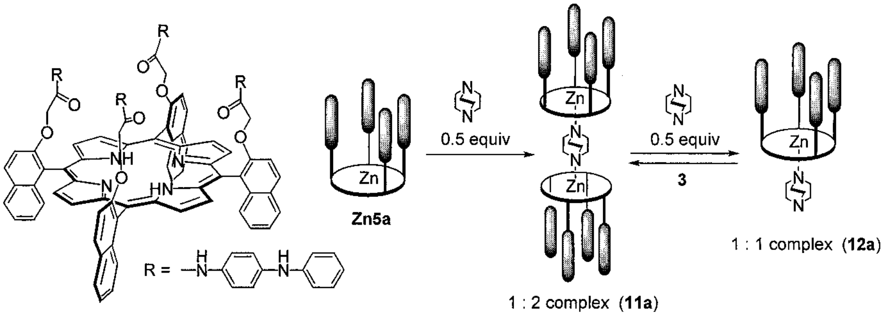
Scheme 2.

Zinc Porphyrins Bearing Four Phenylenediamine Pendant Groups

Zinc porphyrins have been utilized in a variety of host-guest systems[9] and electron- or energy-transfer systems.[10] An additional functionality is allowed to be introduced to the vacant axial coordination site of zinc porphyrins. Use of a bidentate ligand as a secondary bridging spacer is considered to form a sandwich dimer-type zinc porphyrin-ligand complex.[11] According to this type of molecular design, a dimensionally ordered π-conjugated system, in which the central porphyrin–bridging ligand–porphyrin moiety is surrounded by π-conjugated pendant groups, is envisioned to be constructed by using the porphyrins bearing four oriented phenylenediamine strands.

The zinc complex **Zn5a** is quantitatively formed by treatment of **5a** with zinc(II) acetate dihydrate. In the zinc complexation, a zinc(II) species is likely to be introduced selectively from the side opposite to the phenylenediamine strand side because the corresponding αβαβ atropisomer **5b** is metallated with less efficiency in a lower yield. A similar structural circumstance of the pendant groups is indicated as observed with **5**.

The similar four-pendant group effect is observed as described in the case of the free base **5** and **8**. The oxidation potential of the phenylenediamine pendant groups of **Zn5a** (+ 0.29 V vs Fc/Fc$^+$), which is not changed by complexation, was more cathodic than that of **Zn8** (+0.38 V). The fluorescence emission of the porphyrin moiety of **Zn5a** is quenched with more ease than that of **Zn8**.



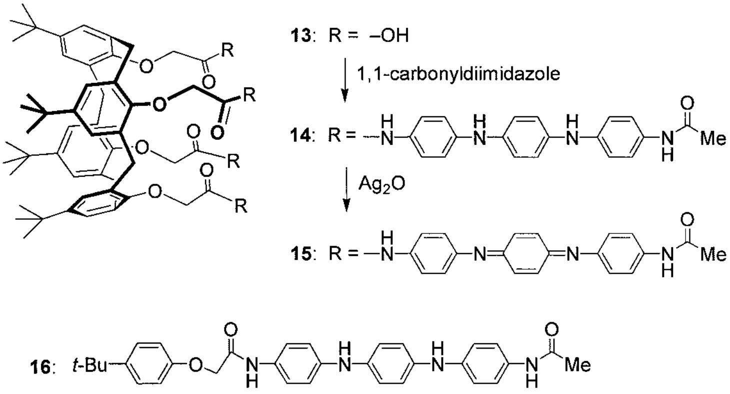
Scheme 3.

The αααα complex **Zn5a**, in which four pendant groups are located on one side of the porphyrin plane, is considered to accommodate a coordination ligand on the other side.[8,12] Diazabicyclooctane (DABCO) is used here as a bridging ligand because of relatively strong basicity. The addition of 0.5 molar equiv of DABCO affords the 2 : 1 complex **11a** with the proximity of two porphyrin π-planes (Scheme 3). Use of 1.0 molar equiv of DABCO results in the formation of the 1 : 1 complex **12a**. It should be noted that the further addition of **Zn5a** to the solution of **12a** leads to the reversible formation of **11a**.

Calix[4]arenes Bearing Four Redox-Active π-Conjugated Pendant Groups

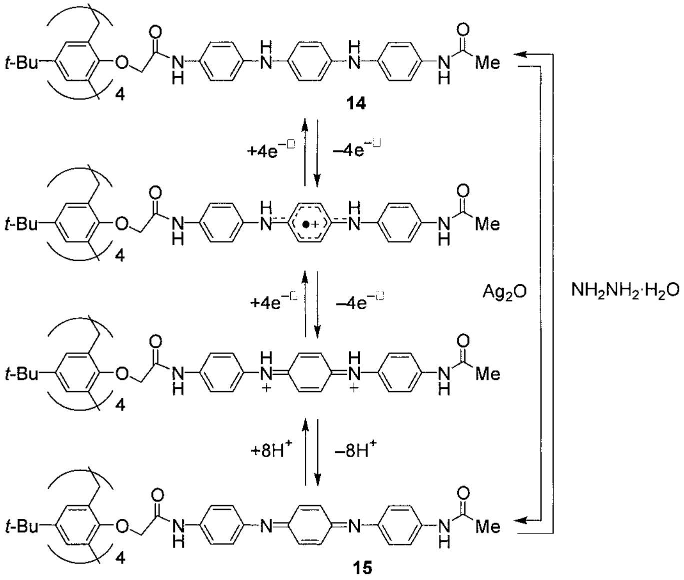
The preorganized macrocyclic conformation of calixarenes has been employed for supramolecular systems, such as molecular capsules,[13] rotaxanes, and catenanes.[14] Calix[4]arene is envisaged to be a scaffold for constructing a dimensionally oriented π-conjugated electronic system, which is considered to be promising for potential applications to, for example, redox-switching receptors and efficient catalysts.[15]

Introduction of *N*-(4-acetylaminophenyl)-*N'*-(4-aminophenyl)-1,4-phenylenediamine (**3**) to 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene (**13**)[16] affords the calix[4]arene **14** bearing four phenylenediamine pendant groups on the lower rim via the corresponding acylimidazolide as shown in Scheme 4.[17] A restricted conformation of the pendant groups is observed spectroscopically.



Scheme 4.

The oxidation states of the redox-active phenylenediamine pendant groups of **14** could be interconverted chemically. The treatment of **14** with Ag_2O in DMF at room temperature results in the oxidation of the phenylenediamine moieties to the quinonediimine ones to afford the calix[4]arene **15** quantitatively, which bears four quinonediimine pendant groups (Scheme 5). The conversion from **14** to **15** is also monitored spectroscopically. As the oxidation reaction proceeds, a CT band assignable to the quinonediimine moieties appears at around 500 nm. The reduction is achieved by the addition of $NH_2NH_2{\cdot}H_2O$ to the thus-obtained solution of **15**, leading to a disappearance of the CT band along with the formation of the reduced derivative **14**.



Scheme 5.

The cyclic voltammogram of **14** in THF exhibits two one-electron redox processes attributable to the phenylenediamine moiety at –86 and 328 mV (E_{pa}) vs. Fc/Fc$^+$. These redox potentials are shifted cathodically in comparison with those of **16** (E_{pa}: –2 and +400 mV). This difference might be again due to the presence of the pendant groups on the lower rim. In DMF, two one-electron redox processes appears as one redox couple despite the observation of two one-electron oxidation waves with **16**: [E_{pa} (mV vs. Fc/Fc$^+$): **14** (0.25 mM) -58; **16** (1.0 mM) -48 and +37]. The redox behavior of **14** is assumed to be accounted for by the more facile intramolecular interchain disproportion of the radical cation species of the phenylenediamine pendant groups to the corresponding phenylenediamine and protonated quinonediimine (two-electron oxidized form) derivatives than the intermolecular interaction of **16**.[18]

Conclusion

The porphyrins and the corresponding zinc complexes bearing dimensionally oriented π-conjugated pendant groups are synthesized and characterized. The structural and electronic characteristics depend on the atropisomers. The photoinduced intramolecular electron transfer from the phenylenediamine moiety to the excited singlet state of the porphyrin moiety is demonstrated in both atropisomers. The sandwich dimer complex is formed by further complexation of the zinc porphyrin complex. The phenylenediamine pendant groups are introduced into the lower rim of the calix[4]arene scaffold, providing another dimensionally oriented redox system. These π-conjugated systems are of potential use in a variety of photoreflactive electron transfer systems such as photocatalysis.

Acknowledgment

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