Novel Redox-Active π-Conjugated Systems

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π-Conjugated polymers and oligomers have attracted much attention in the application to electrical materials depending on their electrical properties. Their oxidation states interconvert each other. For example, polyanilines exist in three different discrete redox forms, which include a fully reduced leucoemeraldine base form, a semioxidized emeraldine one, and a fully oxidized pernigraniline one. The properties are considered to permit the construction of a catalytic system for oxidation reaction. Polyanilines and polypyrroles are demonstrated to serve as synthetic metal catalysts under an oxygen atmosphere in the dehydrogenative oxidation.[1] The similar catalysis is also achieved with the quinonediimine derivatives. Two nitrogens of the quinonediimine moiety have been revealed to be capable of participating in the complexation with transition metals. π-Conjugated compounds serve as a redox-active ligand to provide d,π-conjugated complexes.

A variety of redox-active π-conjugated compounds are able to be designed to control the band gap for the desired electrical and optical properties. One of the approaches to the low band gap compounds depends on an alternating sequence of donor-acceptor units in the π-conjugated molecular chain.

Introduction of acceptor units like benzothiadiazole into an aniline oligomer chain afforded novel π-conjugated compounds **1**-**3**, which exhibited different redox properties as compared with those of aniline oligomers themselves. Cyclic voltammography indicates that the electrochemical properties were related to the length of the chain and the position of the benzothiadiazole ring.

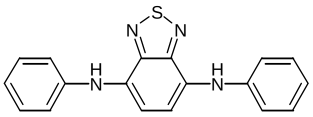
The architecturally ordered orientation and/or assembly of π-conjugated molecular chains are expected to provide three-dimensionally oriented π-electronic systems.

The porphyrins **4** bearing four dimensionally oriented redox-active phenylenediamine pendant groups was constructed to permit the intramolecular photoinduced electron transfer from the phenylenediamine moiety to the porphyrin one.

The sandwich-type π-conjugated systems were constructed by the complexation of the zinc porphyrins **5** bearing the phenylenediamine pendant groups with bridging ligand DABCO. The thus-obtained complexes **6** are considered to provide a unique electronic system, in which the zinc porphyrin as an electron acceptor moiety is surrounded by the electron-donating π-conjugated pendant groups.

Reference

1. T. Hirao, *Coord. Chem. Rev.*, **2002**, *226*, 81-91.



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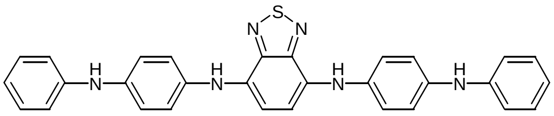

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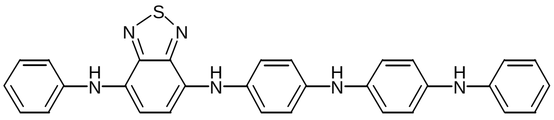

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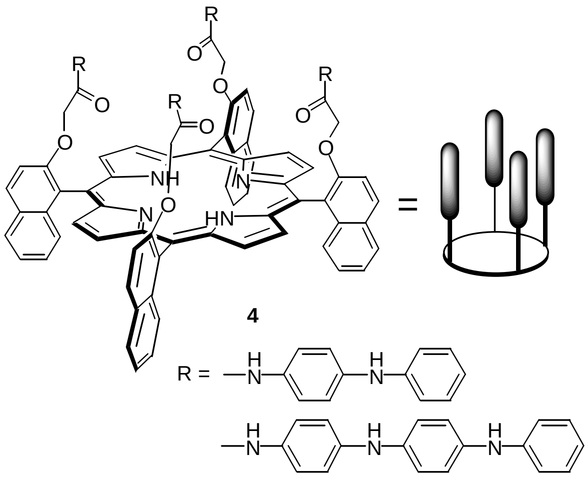

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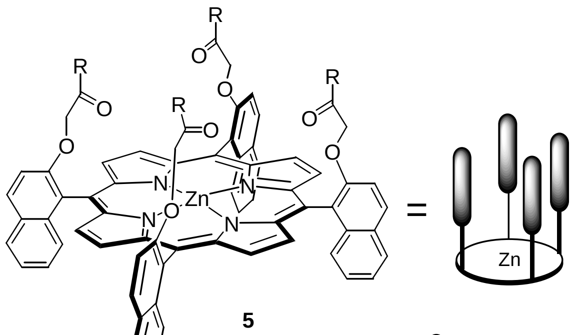

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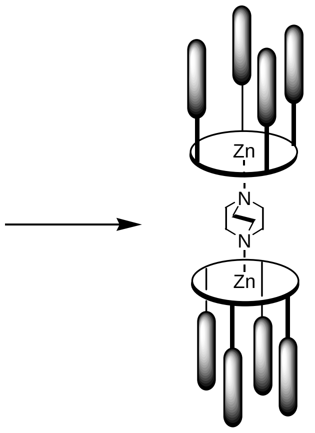

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