

## MACROCYCLIC METAL COMPLEXES AS LADDER POLYMERS

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**Abstract:** Macrocyclic bis-dienes and diendienophile were prepared in Diels-Alder reactions starting from the bis-dienophilic (hemiporphyrinato)nickel complex **1**. Compound **1** was reacted either with the tetraene **2** or with tetraphenylcyclopentadienone (**4**). By combination of macrocyclic bis-dienes and bis-dienophiles, ladder-type oligomers (e.g. **9** or **10**) were synthesized. The described oligomers are precursors for the corresponding conjugated oligomers, which are of interest as organic conductors. The preparation of the corresponding phthalocyanine compounds e.g. **13-16** and a method for obtaining the wanted "D<sub>2h</sub>" phthalocyanine **19** without using tedious methods are reported.

## INTRODUCTION

Ladder polymers have been the targets of many synthetic attempts during the last few years. These double-stranded polymers are expected to show higher mechanical, thermal and chemical stabilities than common single-stranded polymers (Ref. 1). A suitable method to synthesize ladder polymers of high structural regularity is the repetitive Diels-Alder reaction (Ref. 2). It has been shown that macrocyclic metal complexes like phthalocyanines or hemiporphyrazines can be used as bis-dienes or bis-dienophiles in Diels-Alder (DA) reactions (Ref. 3) to prepare such type of polymers.

Thus, the electrical and optical properties of e.g. phthalocyanines (Ref. 4) can be combined with the advantages of ladder polymers. Especially conjugated ladder polymers with macrocyclic subunits containing extended areas of  $\pi$ -electron conjugation are of interest (Ref. 5).

## RESULTS AND DISCUSSION

Convenient phthalocyanine monomers for a repetitive Diels-Alder reaction are accessible through a statistical synthesis starting from two different phthalonitriles (Fig. 1).

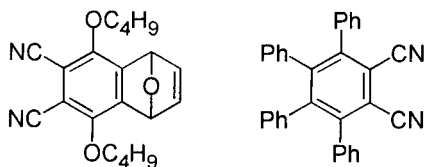


Fig. 1

Unsymmetrically substituted (phthalocyaninato)nickel(II) (PcNi) complexes were synthesized by statistical condensation of a 3,6- or 4,5-substituted dialkoxy- or dialkylphthalonitrile (4,5-dipentyloxy-, 3,6-dihexyloxy-, 4,5-diheptylphthalonitrile) with 3,4,5,6-tetraphenylphthalonitrile and separated by common column chromatography (Ref. 6). Separation by HPLC was successfully used in the case of 1- or 2-alkoxy substituted (phthalocyaninato)nickel(II) complexes (Ref. 7).

The approach of statistical synthesis and separation by HPLC was applied for the preparation of bis-dienophilic phthalocyanines. It was possible for the first time to separate the wanted "D<sub>2h</sub>" phthalocyanine (Fig.2) in its pure form by HPLC as well as by column chromatography from the statistical mixture.

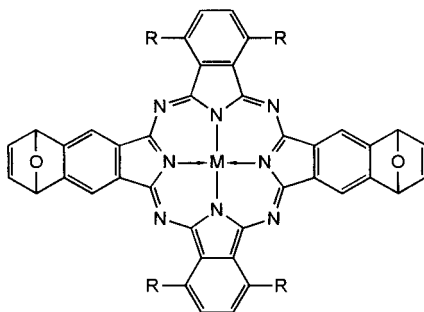


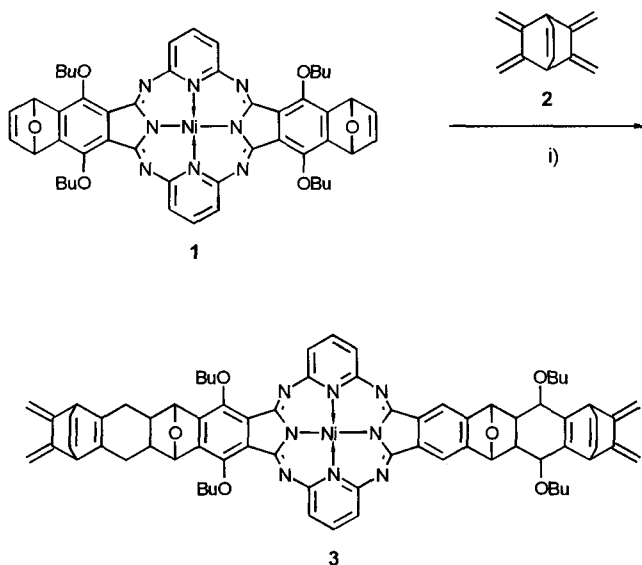
Fig.2

Convenient hemiporphyrizine monomers like **1** (Scheme 1) are more easily accessible. The soluble, bis-dienophilic (hemiporphyrizinato)nickel(II) (HpNi) complex **1** was prepared from the corresponding diiminoisindole, 2,6-diaminopyridine and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (Ref. 8).

The yield was satisfying (31%) and other macrocycles as by-products were only formed in small amounts. **1** is present as a mixture of *syn*, *anti*-isomers due to the relative orientation of the oxygen bridges.

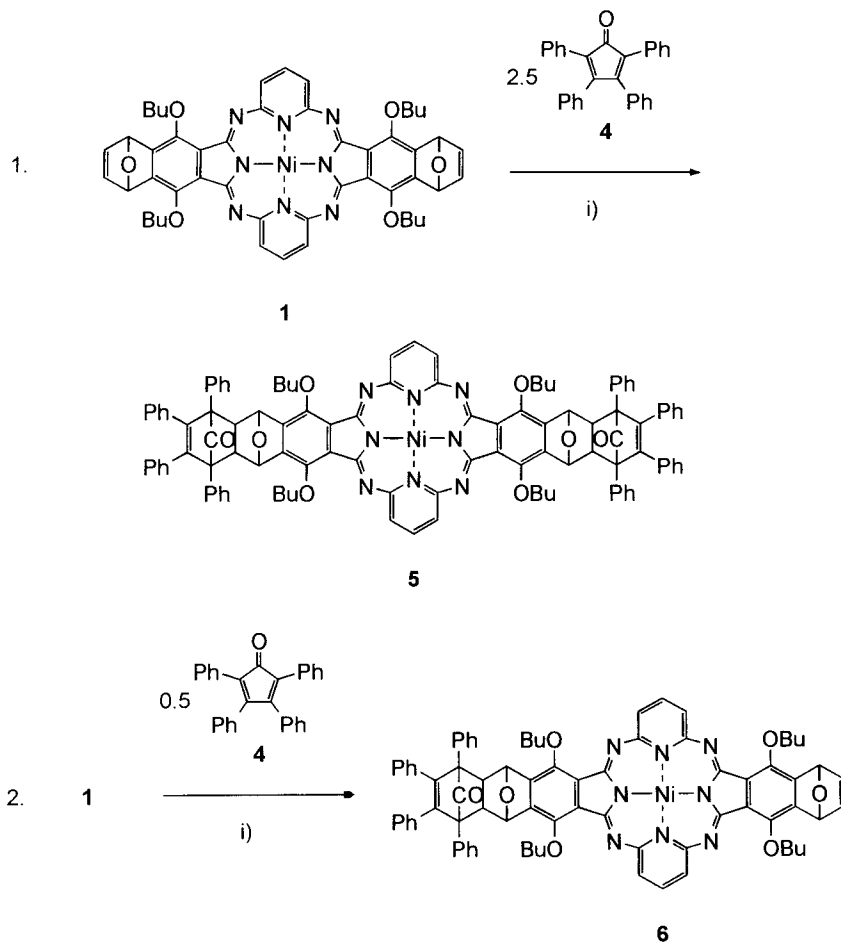
The bis-dienophilic hemiporphyrizine **1** is classified as "AA-monomer". For a polymerisation, complementary bis-dienes ("BB-monomers") are necessary. A repetitive DA reaction can also be carried out starting from a dien-dienophilic ("AB-monomer"). We prepared macrocyclic BB-monomers and an AB-monomer starting from **1** (*syn*, *anti*) in two different ways.

The first strategy consisted of treating **1** with an excess of tetraene **2** (Ref. 9) in boiling toluene. Two DA reactions afforded directly the bis-diene **3** (Scheme 1) in a yield of 57%.



Scheme 1: Synthesis of the macrocyclic BB-monomer **3**. - i): toluene, 110°C, 2.5 equiv. of **2**, 1 h.

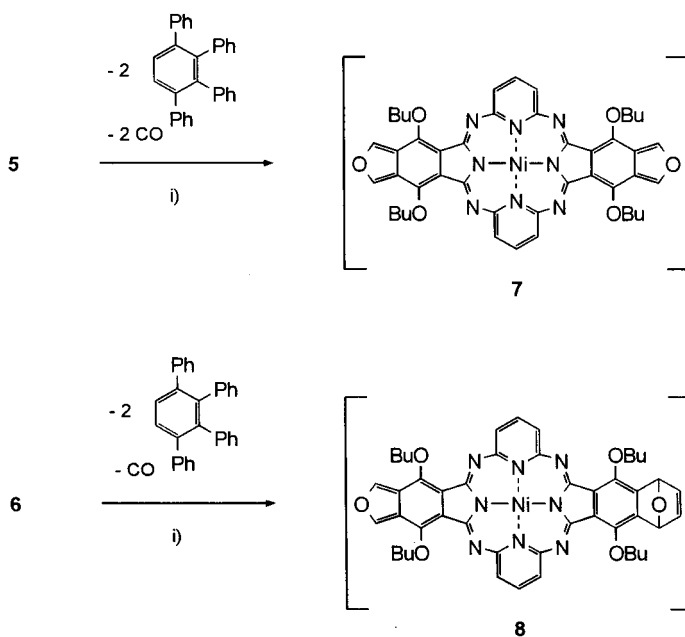
The second pathway to obtain HpNi with diene functions was the conversion of **1** (*syn, anti*) with 1,2,3,4-tetraphenylcyclopentadienone (**4**) in a DA reaction. At 65-70°C the diadduct **5** (starting from 2.5 equiv. of **4**) or the monoadduct **6** (starting from 0.5 equiv. of **4**) were formed (yields 92 and 62% respectively) (Scheme 2). In the synthesis of **6** the diadduct **5** was obtained as a by-product (22%) (Ref. 10).



Scheme 2: Preparation of the BB- and AB-monomer precursors **5** and **6**. - i): toluene, 65-70°C, 24 h.

In the described reactions of **1** (*syn, anti*) with **2** or **4**, several isomers can be formed in each case due to the relative orientation of the bridges and the possible *exo* or *endo* attack in a DA reaction. Since only *exo* addition occurs in both cases, the number of possible isomers is reduced. This fact could be proven from the proton coupling constants in the  $^1\text{H-NMR}$  spectra of **3**, **5** and **6** (Ref. 8,10).

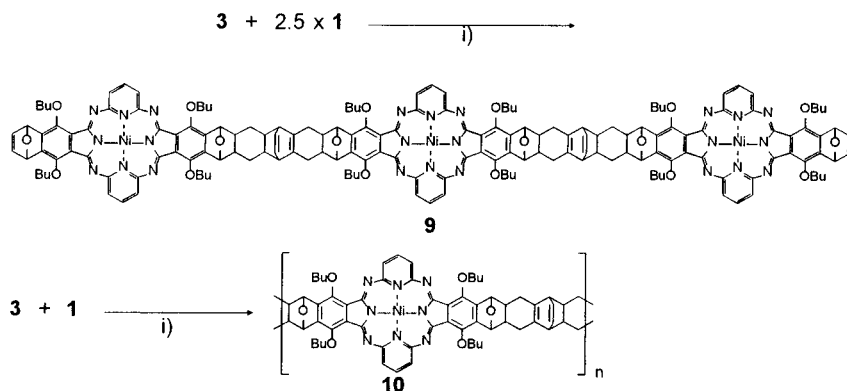
The hemiporphyrazines **5**, **6** are precursor molecules for the reactive intermediates **7** (BB-monomer), **8** (AB-monomer), which were formed *in situ* during heating **5** or **6** in boiling toluene, whereby loss of CO and 1,2,3,4-tetraphenylbenzene occurred (Scheme 3) (Ref. 11). These isobenzofuran intermediates were usually generated in the presence of dienophiles and therefore directly trapped.



Scheme 3: *In situ* formation of the BB- and AB-monomer **7**, **8**. - i): toluene, 110°C, presence of a dienophile.

The mentioned AA-, BB- and AB-monomers proved to be useful as reactive compounds in further DA reactions, e. g. the conversion of **3** with 2.5 equiv. of **1** furnished the HpNi-trimer **9** (Scheme 4). A HpNi-pentamer was built up by functionalizing **9** with excess **2** (as described

for **3**) and allowing the product to react with 2.5 equiv. **1**. Repeating this procedure led to a heptamer and a nonamer (Ref. 4).

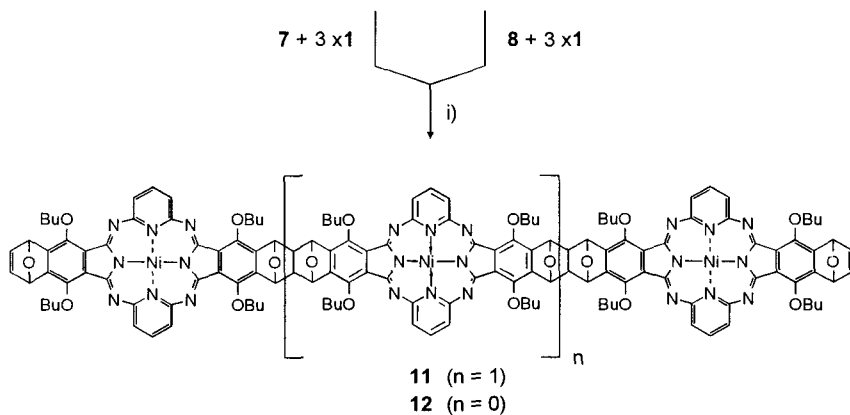


Scheme 4: BB-monomer **3** reacts with an excess of AA-monomer **1** to give the HpNi-trimer **9** and with an equimolar amount of **1** to afford the "polymer" **10**. - i): toluene, 110°C, 7 d.

All oligomers showed good solubility in common solvents like toluene or  $\text{CHCl}_3$  and could therefore be characterized by high-resolution NMR methods. The repetitive DA reaction of equimolar amounts of **1** and **3** afforded the insoluble product **10**. The  $^{13}\text{C}$ -CP/MAS spectrum of this "polymer" is in agreement with the proposed structure (Scheme 4) (Ref. 4).

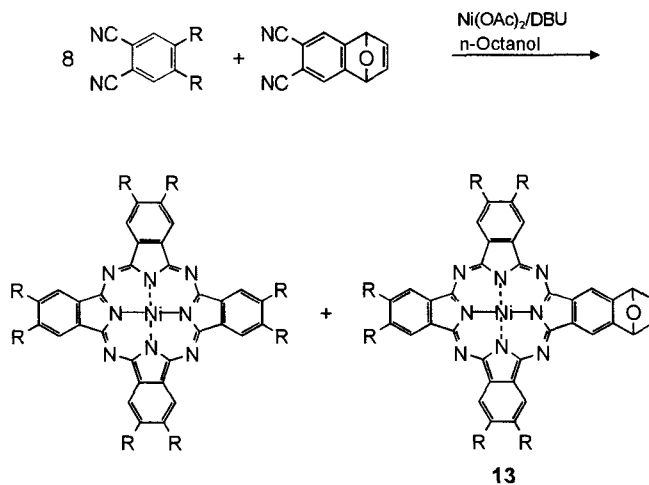
Generation of **7**, **8** in the presence of excess **1** (3 equiv.) delivered the HpNi-trimer **11** and the dimer **12** (Scheme 5), which were also well soluble in common solvents (Ref. 11).

A polymer obtained from **7** and **1** is expected to be superior to polymer **10**: After an aromatisation sequence, the hypothetical conjugated polymer would contain tetracene fragments compared with heptacene fragments in case of the successful aromatisation of **10**. Acenes are known to become less stable with an increasing number of rings. Moreover, small distances between the macrocyclic units are desirable considering the extension of  $\pi$ -electron delocalisation in a conjugated ladder polymer.



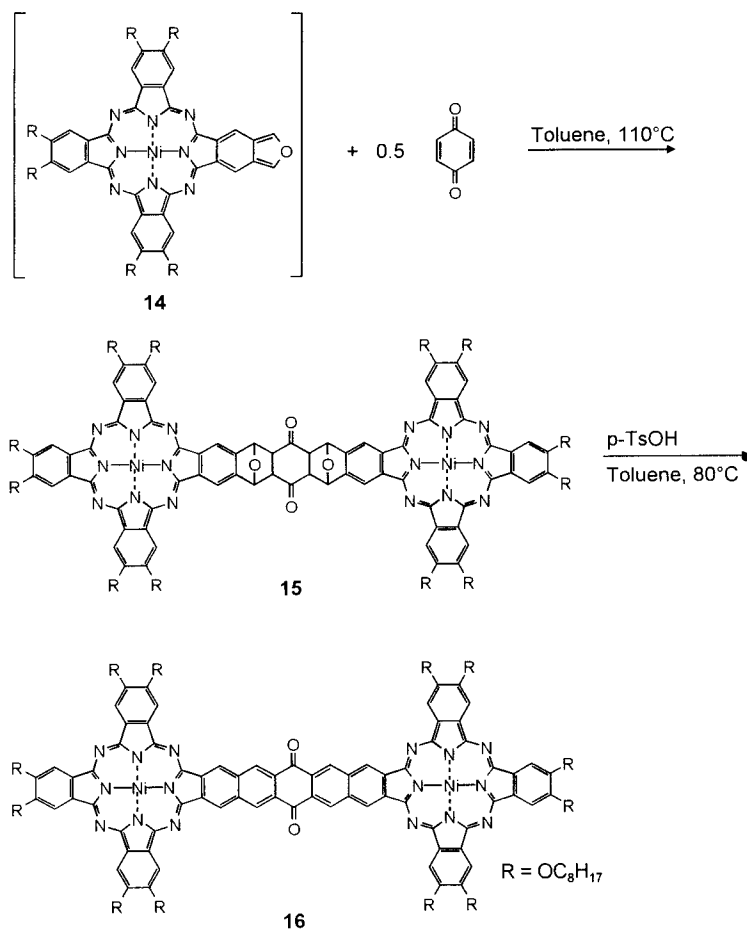
Scheme 5: Synthesis of the soluble HpNi-oligomers **11** and **12** via the "isobenzofuran" strategy. - i): toluene, 110°C, 24 h.

Scheme 6 shows the synthesis of a dienophilic phthalocyanine **13** which could be easily isolated because one of the dinitriles was used in excess.



Scheme 6: Synthesis of **13**

The synthesis of a dienophilic phthalocyanine intermediate suitable for DA reactions can also be done with phthalocyanine precursors leading to the intermediate isobenzofuran derivative **14**. The reaction of **14** with *p*-benzoquinone leads to the dimer **15** which was converted into the conjugated system **16**.

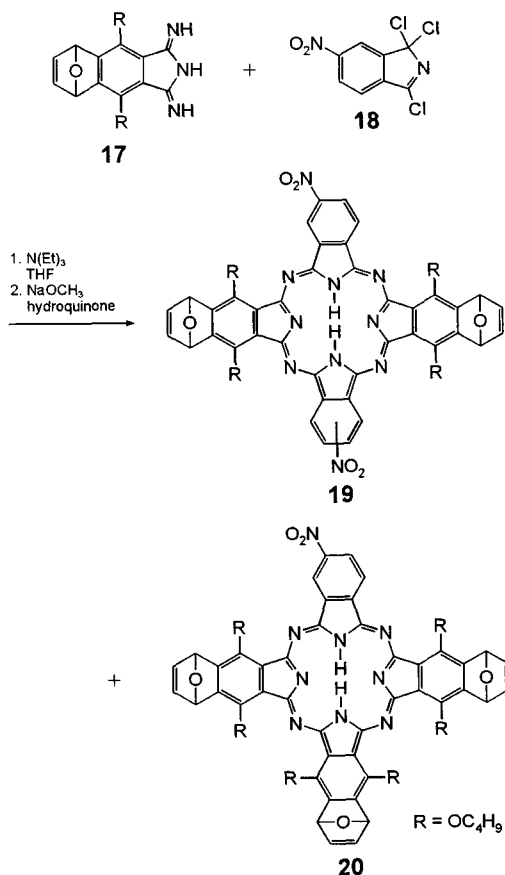


Scheme 7: Synthesis of a ladder-type phthalocyanine dimer

A more direct method for the synthesis of bis-dienophilic phthalocyanines is described in Scheme 8. The obtained yields of the desired bifunctional phthalocyanines are much higher



than those achievable using the statistical approach. Moreover, the isolation of **19** is easier compared with the separation of a statistical mixture, since only one additional phthalocyanine is formed as a minor by-product (Ref. 12). The synthesis of **19** was accomplished by a cross-condensation of the diiminoisoindoline **17** with an equimolar amount of 1,3,3-trichloro-6/7-nitroisoindolenine **18** (Scheme 8) following a procedure first reported by Young and Onyebuagu (Ref. 13).



Scheme 8: Synthesis of a bis-dienophilic phthalocyanine **19**

As mentioned above, the statistical condensation of two differently substituted diiminoisoindolines generally furnishes six phthalocyanines. However, the condensation of **18**

and a substituted diiminoisindoline should give only the "D<sub>2h</sub>" phthalocyanine **19**. The reason for the exclusive formation of a single phthalocyanine is that **18** cannot undergo self-condensation and the selfcondensation of **17** is also suppressed because of the low reaction temperature (0-20°C) used.

## ACKNOWLEDGEMENTS

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