A Novel Route to Ladder-type Structures based on Hemiporphyrazines

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Ladder oligomers with two or three nickel hemiporphyrazine units are synthesized *via* Diels–Alder reaction, using intermediates with isobenzofuran moieties as diene components.

The synthesis of conjugated ladder polymers is interesting not only from a preparative point of view[1] but also because of the potential applications of such polymers as semiconductors or nonlinear optical materials.[2] MO calculations based on extended Hückel theory predict intrinsic conductivity for a planar, fully conjugated metallophthalocyanine polymer with a ladder-type structure.[3] Until now, the best route to obtain double-stranded polymers of high structural regularity is the repetitive Diels–Alder reaction.[4] We recently reported the usage of macrocycles in Diels–Alder reactions,[5] especially the synthesis of a ladder polymer starting from nickel hemiporphyrazine complexes [Ni(hp)] as monomers.[6] Convenient Ni(hp) monomers for polymerisation *via* repetitive Diels–Alder reaction are more easily accessible than the analogous phthalocyanines.[7]

In this paper, we report the synthesis of the Ni(hp)-dimer **3a** and the Ni(hp)-trimers **5a,b** (Scheme 1) starting from the monomer precursors **6** and **7a,b** (Scheme 2). For the first time, a Diels–Alder reaction between macrocyclic units was carried out by using the intermediates **1a** and **4a,b** as diene components. These intermediates were generated from the precursors **6** and **7a,b** (Scheme 2) in the presence of an excess of the Ni(hp) **2a** or **2b** to form the dimer **3a** and the trimers **5a,b** respectively (Scheme 1). The used hemiporphyrazines **2a** and **2b** are mixtures of *syn* and *anti* isomers, where *syn* or *anti* refers to the orientation of the oxygen bridges. The syntheses of **2a** and **2b** are described in ref. 8. The ladder-type compounds **3a** and **5a** show good solubility in $CHCl_3$ or THF, while the trimer **5b** is almost insoluble in common organic solvents. This is due to the lower number of side-chains in **5b** compared with **5a** (Scheme 1).

The AB-'monomer' **1a** and the BB-'monomers' **4a,b** are formed *in situ* by stirring the precursor molecules **6** or **7a,b** in refluxing toluene (Scheme 2), whereby loss of CO and 1,2,3,4-tetraphenylbenzene leads to the formation of the reactive intermediates **1a** or **4a,b**, which are trapped in the presence of dienophiles.[9,10]

The precursors **7a,b** were obtained in yields of 90% (**7a**) and 92% (**7b**) by the reaction of 2.5 equiv. of tetraphenylcyclopentadienone with the Ni(hp) **2a,b** in toluene at 65 °C in a nitrogen atmosphere. Complete conversion of **2a,b** was monitored by TLC (silica gel, CH_2Cl_2–ethyl acetate 4 : 1). Precursor **6** was synthesized under the same conditions, starting from 0.5 equivalents of tetraphenylcyclopentadienone. The main product **6** (62% yield) was separated from **7a** (22% yield) and the excess of **2a** by column chromatography on silica gel with CH_2Cl_2–ethyl acetate (5 : 1) as eluent.

In a typical procedure, the dimer **3a** and the trimers **5a,b** were synthesized in the next step by stirring an appropriate precursor with a threefold excess of the corresponding bis-dienophile in refluxing toluene (nitrogen atmosphere, **3a**, **5a**: 24 h; **5b**: 3 days) (Scheme 1). The insoluble trimer **5b** precipitated from the reaction mixture and was extracted with toluene and $CHCl_3$ to achieve purification (53% yield). The soluble products **3a**, **5a** were separated from the excess of **2a** by column chromatography (silica gel, CH_2Cl_2–THF 2 : 1) and then extracted with ethyl acetate. The isolated yields were 62% (**3a**) and 66% (**5a**).

The structures ascribed to **3a** and **5a** were mainly proved by high-resolution ^1H and ^{13}C NMR spectroscopy (Fig. 1).† NMR data of the insoluble trimer **5b** could be obtained by ^{13}C CP MAS spectroscopy.‡

In previous work, only *exo*-addition was observed in the Diels–Alder reaction of isobenzofurans with 1,4-epoxynaphthalenes.[9,10] Due to this observation, the arrangement of adjacent oxygen bridges in **3a** and **5a,b** should either be *exo/syn* or *exo/anti*. Our NMR data are consistent with these two possible arrangements. For example, in the ^{13}C NMR spectrum of the isomeric mixture **5a** signals derived from C-2b, C-2c appear at δ 75.7, 78.5 (*exo/anti*) and at δ 79.6 (*exo/syn*).§ The appearance of five resolved peaks for C-3b, -3c and C-4b, -4c seems also to be due to the different arrangements. For C-1b, only one signal is found at δ 49.9. The assignments shown in Fig. 1 are based on the knowledge of the NMR data of the monomer **2a**[8] and were furthermore confirmed by DEPT and C–H–COSY spectra. In the ^1H NMR spectrum, characteristic signals appear as broad singlets at δ 5.00, 5.52 (H-2b, H-2c, *exo/anti*) and 5.62 (H-2b, H-2c; *exo/syn*). Proton H-1b gives rise to two peaks with different intensities (δ 2.20: *exo/syn*, 2.87: *exo/anti*). In order to determine the ratio of *exo/syn* to *exo/anti* arrangements in **3a** and **5a**, the signal intensities of the mentioned proton peaks were compared. In both cases, we obtained a ratio of *exo/syn* : *exo/anti* ≈ 1 : 5.

The ^1H and ^{13}C chemical shifts of the dimer **3a** show almost no deviation from those of **5a**. The relations of peak intensities in the ^1H NMR spectrum are consistent with the proposed structure.

In the solid-state NMR spectrum of **5b**, characteristic ^{13}C NMR shifts are found at δ 50 (C-1b), 77 and 80 (C-2a, -2b, -2c). Further signals are in agreement with the ^{13}C NMR data of monomer **2b**.[8]

Mass determination of the soluble compounds **3a**, **5a** was carried out by FAB MS. The M^+ peaks at 1809 (**3a**) and 2702 (**5a**) are the most intense peaks in the regions between *m/z* 1000 and 3000 of the spectra. Peaks with higher *m/z* values appear in both cases and can be explained by addition of the intermediates **1a** and **4a** to the dimer **3a** or the trimer **5a**, respectively. These intermediates may be generated in the mass spectrometer by retro-Diels–Alder reaction.

Our future interest will focus on using the described way to synthesize higher oligomers and polymers based on hemiporphyrazines. The development of strategies to achieve aromatisation of these ladder structures is in progress.

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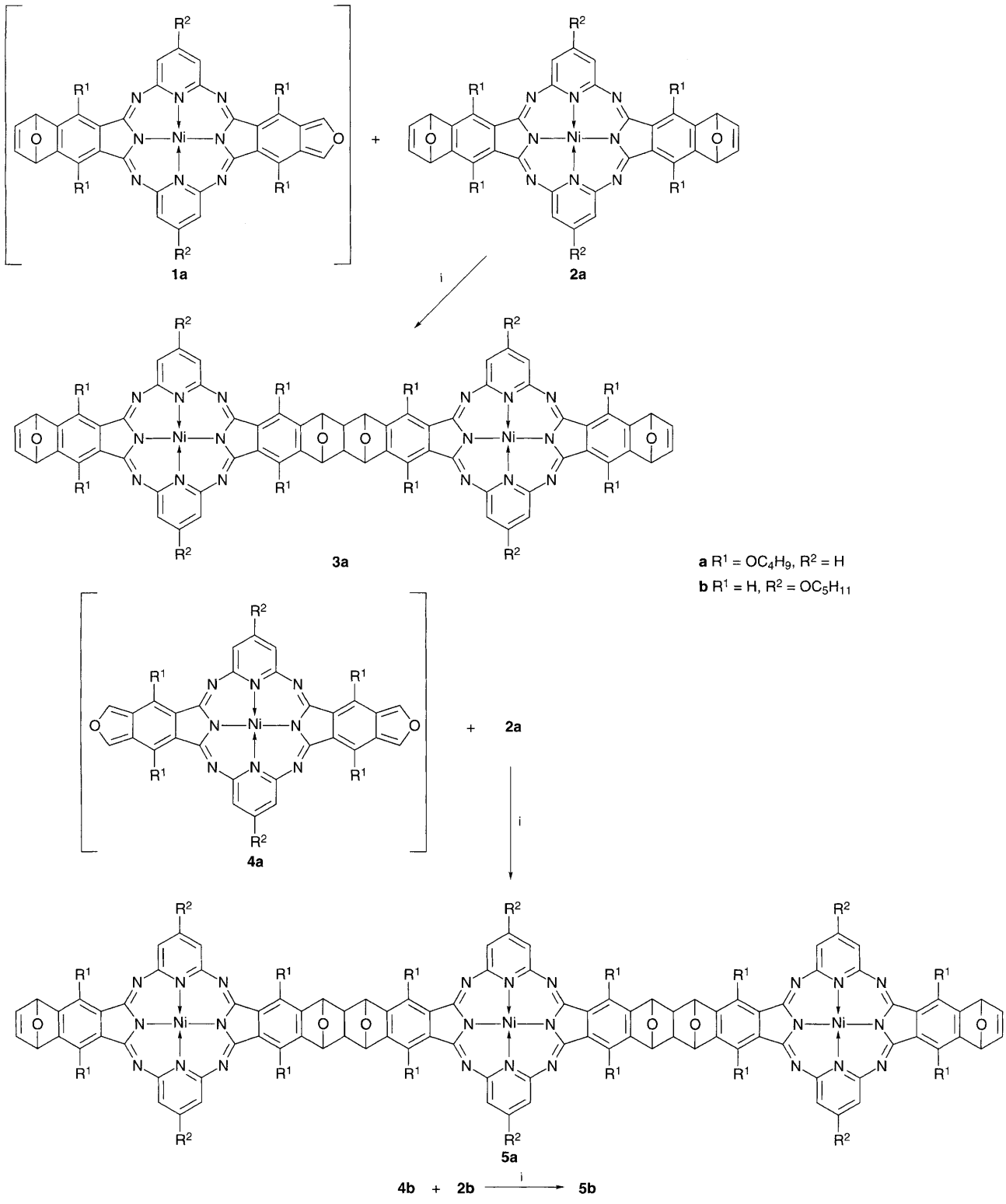
Footnotes

† Satisfactory spectroscopic and analytical data were obtained for all new compounds. *Selected spectroscopic data*: **5a**; IR ν/cm^{-1} (KBr) 2957, 2932, 2870, 1663, 1612, 1576, 1537, 1489, 1435, 1393, 1204, 1161, 1065, 893, 810, 722; FAB MS *m/z* 2702 (M^+ + H), 1784 (M^+ − **2a**), 3569, 4489; ^1H NMR (250 MHz, $CDCl_3$) δ 0.95 (36 H, m, CH_3), 1.49 (24 H, m, CH_2), 1.74 (24 H, m, CH_2), 2.20, 2.87 (4 H, s, H-1b), 4.01–4.25 (24 H, m, OCH_2), 5.00, 5.52, 5.62 (8 H, s, H-2b, -2c), 5.90 (4 H, s, H-2a), 6.49 (12 H, m, H-8a–c), 7.01 (4 H, s, H-1a), 7.39 (6 H, m, H-9a, -9b); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.9, 14.0 (CH_3), 19.1, 19.3 (CH_2), 32.1, 32.2 (CH_2), 49.9 (C-1b), 74.5, 74.7 (OCH_2), 75.7, 78.5, 79.6 (C-2b, -2c), 80.7 (C-2a), 120.2 (C-8a–c), 129.2, 129.5, 129.9 (C-5a–c), 139.3 (C-9a, -9b), 142.5 (C-1a), 141.0, 143.2, 143.4, 143.6, 144.0 (C-3b, -3c, -4b, -4c), 144.4 (C-4a), 145.7 (C-3a), 155.6, 155.7, 156.0 (C-6a–c), 158.0 (C-7a–c). **3a**; FAB MS *m/z* 1809 (M^+), 891 (M^+ − **2a**), 2700 (M^+ + **1a**); IR absorptions and ^1H and ^{13}C chemical shifts show only small deviation from the values listed above for **5a**.



Scheme 1 *Reagents and conditions*: i, toluene, reflux

‡ *Selected spectroscopic data* for **5b**: IR ν/cm^{-1} (KBr) 2953, 2926, 2868, 1628, 1578, 1528, 1431, 1364, 1315, 1215, 1184, 1126, 1030, 868, 743, 619; ^{13}C CP MAS NMR (75.5 MHz) δ 13 (CH_3), 22 (CH_2), 28 (2 CH_2), 50 (C-1b), 68 (OCH_2), 77, 80 (C-2a–c), 104-112 (C-4a–c, -8a–c), 137 (C-5a–c), 144-150 (C-1a, -3a–c), 158 (C-6a–c, -7a–c), 167 (C-9a, -9b).

§ For NMR data of related compounds see refs. 9 and 10.

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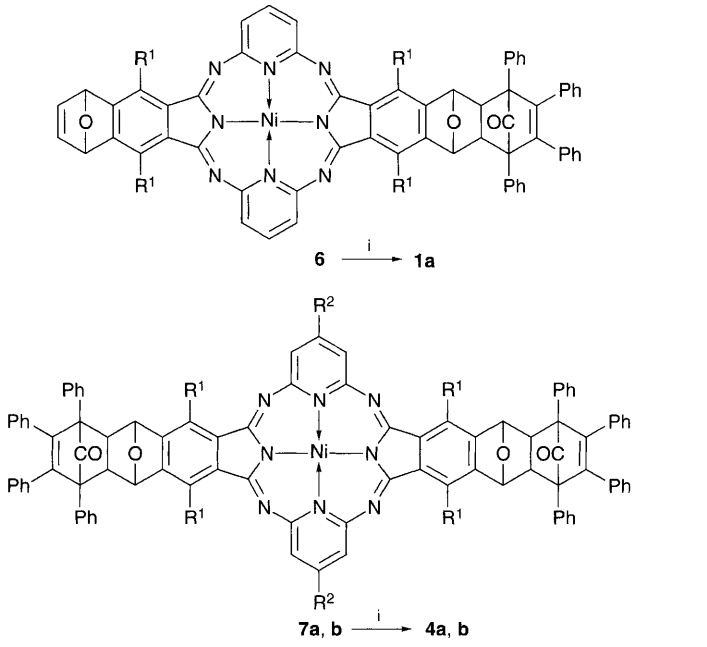

Scheme 2 *Reagents and conditions*: i, toluene, reflux

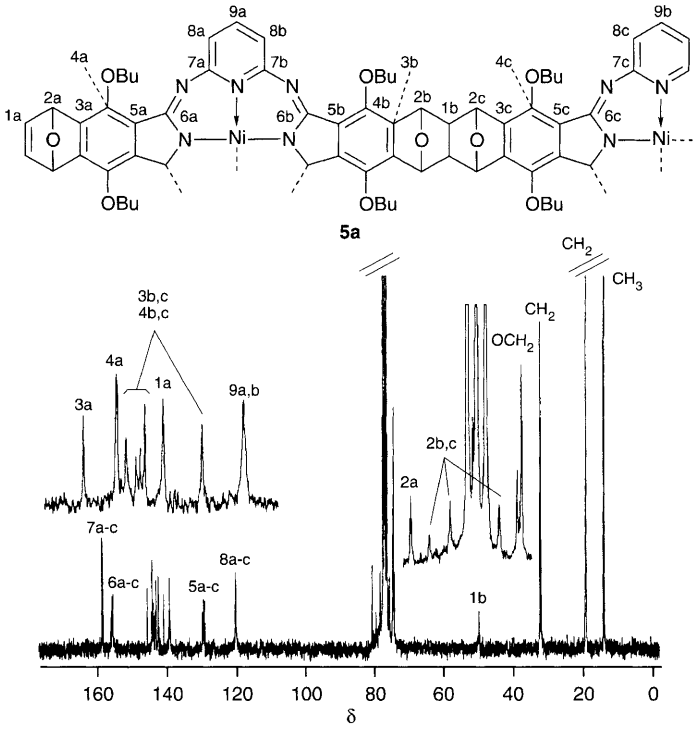

Fig. 1 ^{13}C NMR spectrum of trimer **5a** ($CDCl_3$)

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