Influence of Substituents, Reaction Conditions and Central Metals on the Isomer Distributions of 1(4)-Tetrasubstituted Phthalocyanines

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Abstract: The 1(4)- and 2(3)-tetraalkoxy-substituted nickel (**5**), copper (**6**), and metal-free phthalocyanines **7** and **8** were synthesized from the corresponding substituted phthalonitriles **2** and **4,** respectively, and the four structural isomers formed for each phthalocyanine were separated by HPLC. In the case of 1(4)-tetraalkoxy-substituted phthalocyanines, the ratio of the four isomers was found to be different from the expected statistical distribution of D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5. For the 1(4)-substituted metal-free phthalocyanine **7** a very high proportion of the C_{4h} isomer (87%) is formed. In the case of the 1(4)-substituted metal phthalocyanines **5** and **6** the strikingly low proportion of the D_{2h} isomer (found: 2–4% compared to statistical distribution: 12.5%) is interpreted by a template mechanism (given in Scheme 2) in which strong steric hindrance of the respective neighboring groups prevent the formation of the D_{2h} isomer. To investigate further the mechanism of formation of phthalocyanines the synthesis of 1(4)- and 2(3)-tetraalkoxy-substituted metal phthalocyanines containing chiral alkoxy groups (**13–17**) was studied under different reaction conditions starting from the corresponding alkoxy-substituted phthalonitriles **10** and **11**. In all investigated cases the chiral alkoxy groups in the starting phthalonitrile again affect the distribution of the structural isomers of the formed phthalocyanines, leading to a higher proportion of the C_{4h} isomer in comparison with the 1(4)-tetraalkoxy-substituted phthalocyanines with racemic alkoxy groups.

Keywords: chirality · dyes · isomer separation · phthalocyanines

Introduction

Phthalocyanines, commonly used as dyes or catalysts, have recently undergone an enormous renaissance.[1a] This is mainly due to the fact that phthalocyanines, metal phthalocyanines, and many of their substituted derivatives exhibit properties that are interesting for many applications, especially in material science.[1] Phthalocyanines, metal phthalocyanines, and peripherally substituted, for example tetra-, octa-, and hexadeca-substituted, phthalocyanines are normally synthesized starting from the appropriate phthalonitriles or diiminoisoindolines.[1a] In spite of the large number of different phthalocyanines and metal phthalocyanines, which have been synthesized in recent years, the mechanism of formation of phthalocyanines and their derivatives starting from phthalonitriles or diiminoisoindolines is still not clear and under debate. Several mechanistic pathways which depend upon the reaction conditions have been proposed.[2–5]

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Herein, we report on a new approach to study the mechanism of formation of phthalocyanines by investigating the different ratios of structural isomers of tetrasubstituted phthalocyanines and metal phthalocyanines that are formed from substituted phthalodinitriles or substituted diiminoisoindolines[6] depending upon the reaction conditions (solvent, temperature, and metal salt). The separation of structural isomers of formed phthalocyanines and the study of the influence of the substituents on the distribution of the structural isomers are important factors for gaining more information about the mechanism of the phthalocyanine formation.

These investigations were possible because we were recently able for the first time to separate the four structural isomers of 1(4),8(11),15(18),22(25)-[7, 8] and 2(3),9(10), 16(17),23(24)-tetraalkoxy-substituted[8] nickel phthalocyanines[6] (Figure 1), which are formed from the corresponding 1(4)- and 2(3)-alkoxy-substituted phthalonitriles and nickel salts. Their characterization in terms of their symmetry was carried out by ^{1}H NMR and UV/Vis spectroscopy.

From this work[6, 7] it became clear that in the case of the formation of 2(3)-substituted nickel phthalocyanines (Figure 1) the mechanism follows a strong statistically controlled route irrespective of the size of the substituents. In other words, in the investigated examples the structural isomers D_{2h}, C_s, C_{2v}, and C_{4h} were always formed in a ratio of

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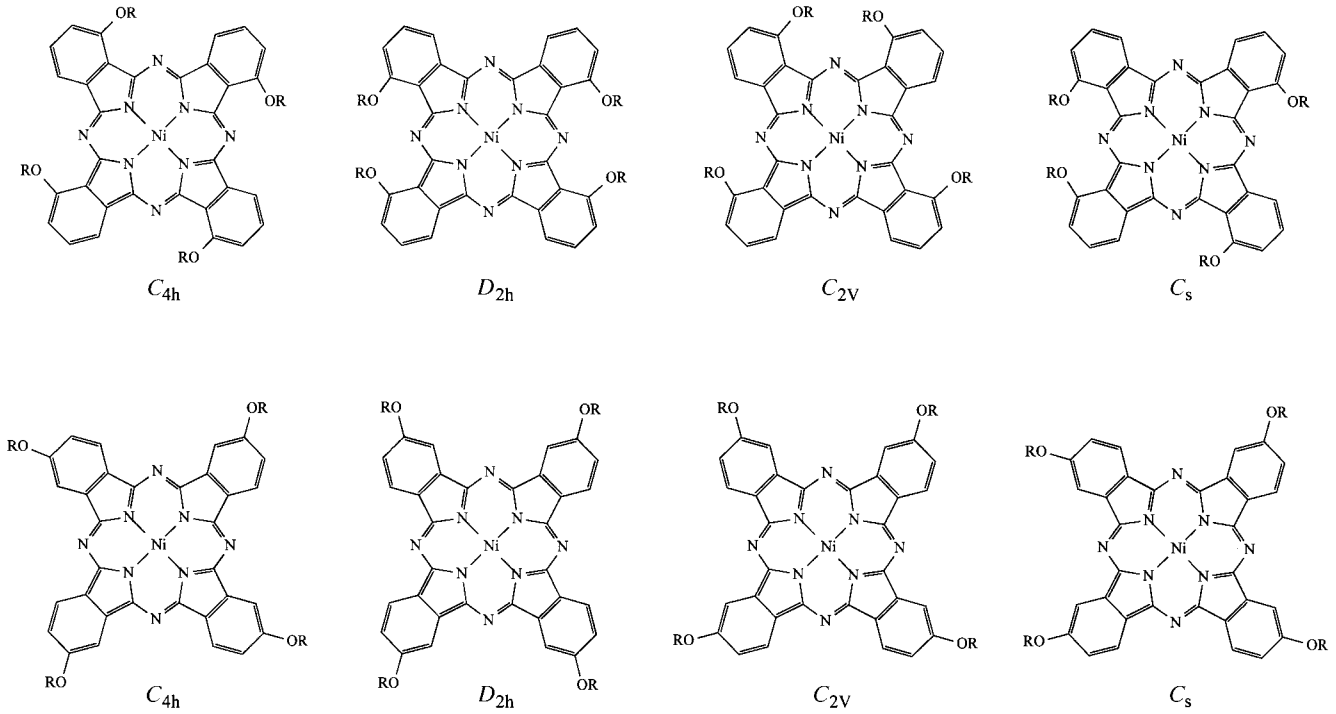


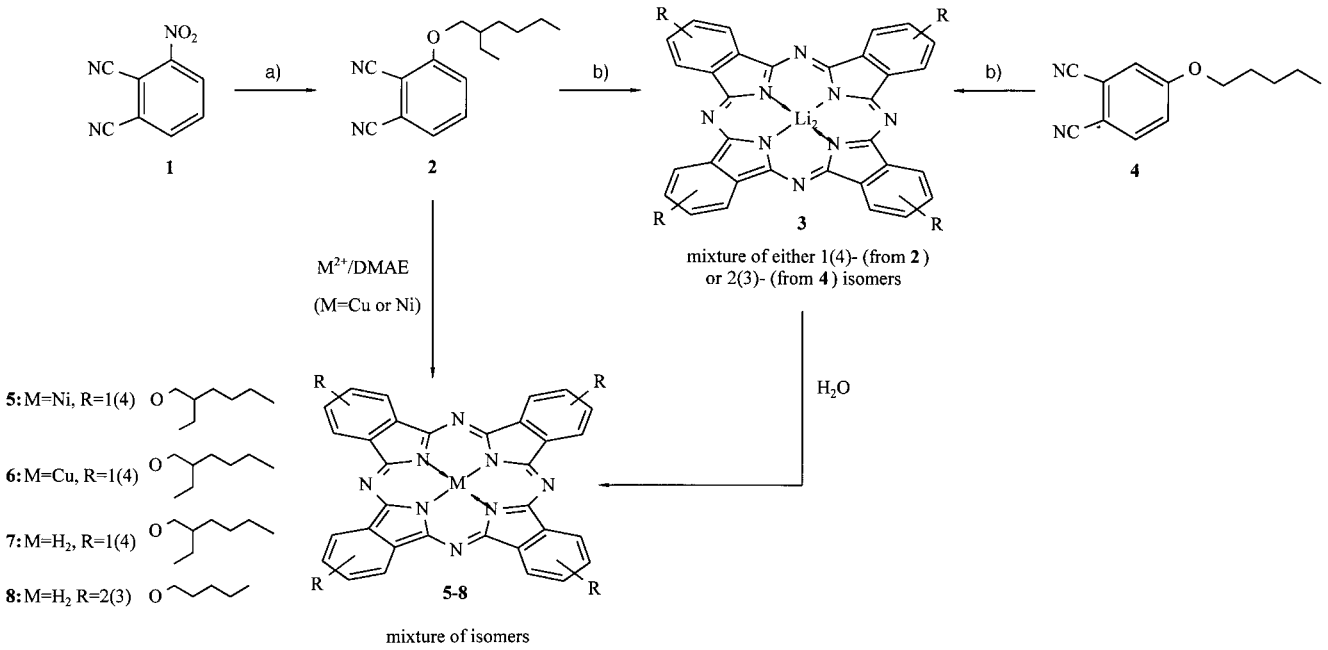
Figure 1. Structures of 1(4)- (top) and 2(3)-tetrasubstituted nickel phthalocyanines (bottom).

12.5:50:25:12.5. This was not the case for the 1(4)-tetrasubstituted nickel phthalocyanines (Figure 1). In this case, a strong influence of the substituents on the isomer distribution was observed for the formation of the corresponding 1(4)-tetrasubstituted nickel phthalocyanines.[6] This was explained with the specific interactions of the substituents in the process of formation of the nickel phthalocyanines from the substituted phthalonitriles.

In the present work, we report more detailed studies about the formation and distribution of the structural isomers of 1(4)- and 2(3)-tetraalkoxy-substituted metal and metal-free phthalocyanines starting from the corresponding respectively substituted phthalonitriles (see Scheme 1). The synthesis of the alkoxy-substituted phthalocyanines was carried out by reacting the corresponding alkoxyphthalonitrile **2** with different metal salts. The corresponding metal-free phthalocyanines **7**, **8** were obtained by reacting the alkoxyphthalonitriles **2** and **4** with lithium in pentanol. The influence of chiral substituents in the starting phthalonitriles on the product distribution of the tetrasubstituted phthalocyanines was also studied for the first time.

Results and Discussion

For a systematic study of the structural isomer distribution in tetrasubstituted phthalocyanines, we started with appropriately substituted phthalonitriles such as **2** (Scheme 1) and studied the formation of the corresponding phthalocyanines such as **5** from them depending upon the reaction conditions and the use of the metal salt. The substituted phthalodinitrile **2** was prepared by nucleophilic substitution of the nitro group in 1,2-dicyano-2-nitrobenzene (**1**) with 2-ethylhexyl alcohol in DMF in the presence of K_2CO_3. 1,2-Dicyano-3-(2-ethylhexyloxy)benzene (**2**) was treated with $NiCl_2$ and $CuSO_4 \cdot 5H_2O$, respectively, in 2,2-dimethylaminoethanol for 6 hours at 140 °C to yield 1(4)-tetra-(2-ethylhexyloxy)phthalocyaninatonickel (**5**) and 1(4)-tetra-(2-ethylhexyloxy)phthalocyaninatocopper (**6**), respectively (Scheme 1). In contrast, the metal-free 1(4)-tetra-(2-ethylhexyloxy)phthalocyanine (**7**) was obtained from the phthalocyaninatodilithium compound **3**. The dilithium compound **3** was prepared from **2** by treatment with lithium in 2-ethylhexanol for 6 h at 130 °C (2-ethylhexanol was used as the solvent to avoid an ether ligand exchange). The metal-free macrocycle **7** was prepared by treating **3** with water. All products were purified by column chromatography and afterwards subjected to HPLC chromatography. All experiments were carried out at least three times. The determined isomer ratios differ only within the experimental error of the HPLC analyses. As we have described earlier, the structural isomers (see Figure 1) of the substituted phthalocyanines **5**–**7** were separated by using our earlier described HPLC phases.[6] The symmetry of the separated phthalocyanine isomers was determined by the number of signals in the aromatic region of the ^{1}H NMR spectra and by UV/Vis spectroscopy.[6, 7] The distribution of structural isomers of the 1(4)-tetrasubstituted phthalocyanines **5**–**8** found for the respective reactions given in Scheme 1 is listed in Table 1. The phthalocyaninatonickel and -copper complexes **5** and **6** were formed with comparable distribution of the respective structural isomers, in contrast to the metal-free phthalocyanine **7** which is formed with a totally different pattern of isomers. In **7** the isomer with the highest symmetry C_{4h}, was formed as the major component (87 %),[9] whereas the proportion of the other isomers decreases and reaches zero for the D_{2h} system. These results of different distribution of



Scheme 1. Synthesis of **5**–**8**. a) $C_8H_{17}OH$/DMF, K_2CO_3; b) Li/$C_8H_{17}OH$

Table 1. Percentage distribution of the four structural isomers in the formation of 1(4)- and 2(3)-tetrasubstituted phthalocyanines (see Scheme 1)

Phthalonitrile	Reaction conditions[a]	Product	Isomer ratio [%][b] D_{2h}	C_S	C_{2v}	C_{4h}
2	$NiCl_2$/DMAE, 6 h/140 °C	**5**	4	50	31	15
2	$CuSO_4 \cdot 5H_2O$/DMAE, 6 h/140 °C	**6**	2	49	4	8
2	Li/$C_8H_{17}OH$, 6 h/130 °C	**7**	–	11	2	87
4	Li/$C_5H_{11}OH$, 3 h/130 °C	**8**	9	71		20

[a] The differences in the temperature and reaction time for the synthesis of 1(4)- and 2(3)-substituted Pcs are based on monitoring of the reaction by thin-layer chromatography. The reaction of 2(3)-substituted metal-free Pc was complete after 3 h at 130 °C. [b] Statistical distribution; D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5.

the structural isomers show that in comparison to the metal phthalocyanines **5** and **6** a different kind of mechanism is operative in the formation of metal-free phthalocyanine **7**.

Smith and Oliver[2] and Borodkin[3] demonstrated that the initial reaction of phthalonitrile with sodium alkoxide leads to the sodium salt of 1-imido-3-alkoxyindoline **I** (Figure 2). If the substituted phthalonitrile **2** is treated with lithium in 2-ethylhexanol, two types of substituted precursors **Ia** and **Ib** could be formed (Figure 2). Semiempirical calculations[10] show that the two cyano groups in **2** are electronically not equivalent. They carry different positive charges on their carbon atoms (Figure 3) and therefore the nucleophilic attack of an 2-ethylhexanolate anion at the CN groups in the 2-position in **2** would lead preferentially to the formation of isoindoline **Ia** (Figure 2). The next step in the reaction sequence is the nucleophilic attack of **Ia** to another phthalonitrile,[2] again at the 2-cyano group. A dimer is formed which can now either react with another phthalonitrile **2** in the same way to form a trimer, etc., or undergoes self-condensation. In both routes the cyclization takes place stereoselectively and the isomer with C_{4h} symmetry is obtained, which is thermodynamically favored.

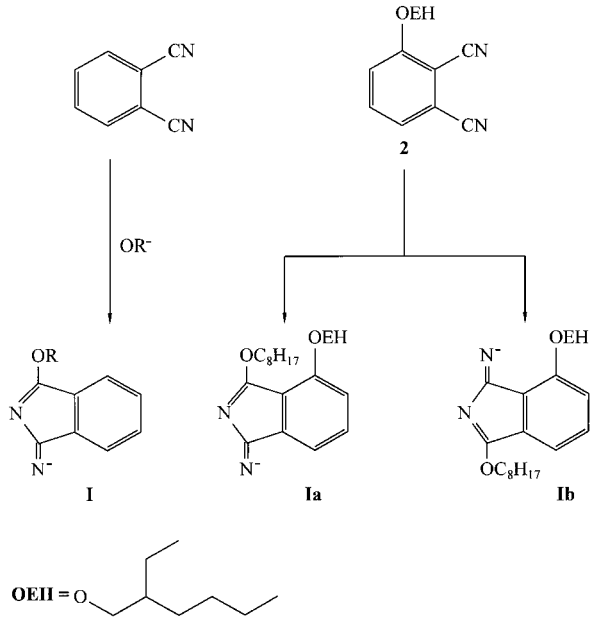


Figure 2. Structures of proposed intermediates **I**, **Ia**, and **Ib**.

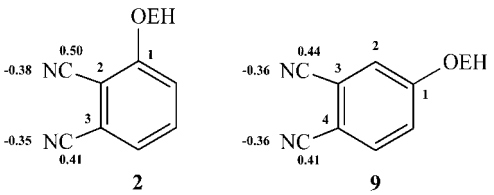


Figure 3. Charge distribution on substitued phthalonitriles **2** and **9**.

Another mechanism must be operative for the formation of the metal phthalocyanines **5** and **6** (Scheme 1). No strong bases such as alcoholates are used for their synthesis and therefore an isoindoline derivative is not necessarily formed. The obtained distribution of structural isomers (Table 1)

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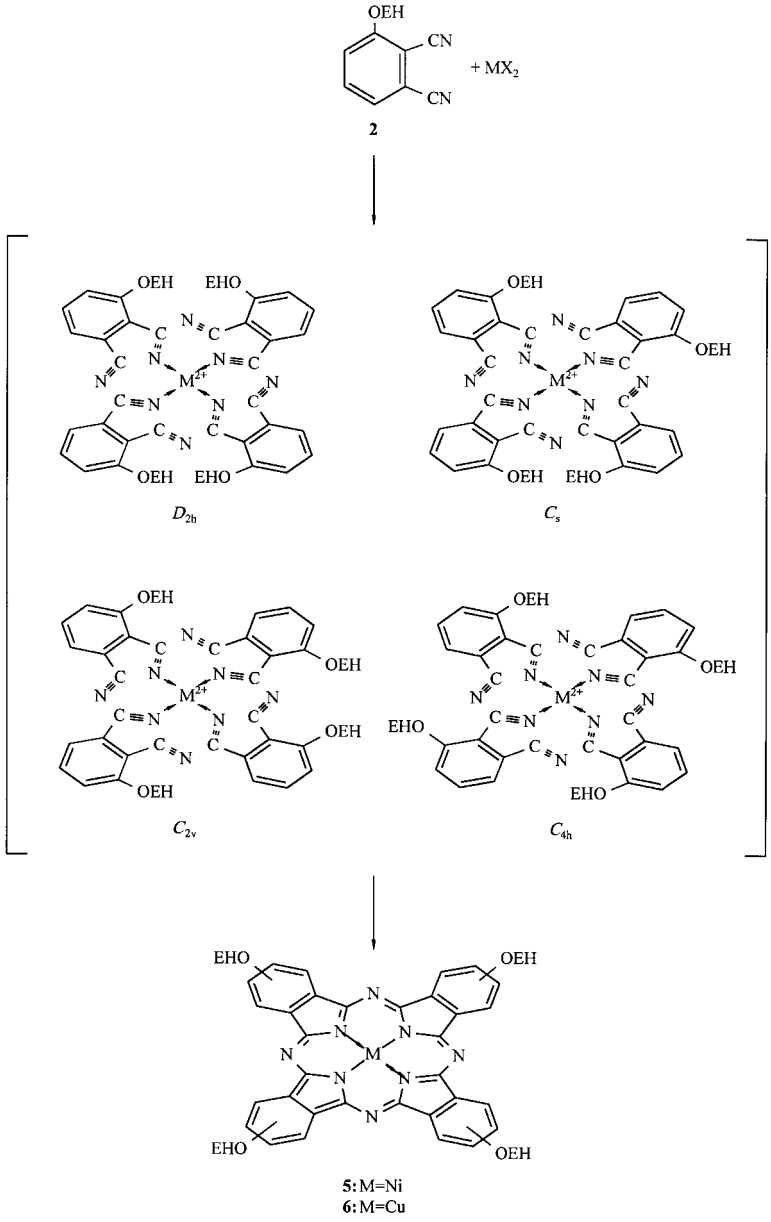
points to a reaction mechanism controlled by a template effect.[5, 11, 12] Four phthalonitrile units coordinate in the first step to the metal ion (Scheme 2). The formation of the phthalocyanine macrocycles can take place starting from these template complexes. Since the phthalodinitriles **2** bind together in a statistical manner (Scheme 2) an isomer distribution of **5** and **6** close to the statistical values (D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5) would be expected. The strikingly low proportion of the D_{2h} isomer in **5** and **6** (4% and 2%, respectively, instead of 12.5%) (Table 1) must be explained by the strong steric hindrance of the respective neighboring alkoxy groups (OEH) which hinders the formation of a D_{2h}-template arrangement of the phthalonitriles **2**. The difference with respect to the ratio of the isomers for Ni and Cu as a central metal atom in the phthalocyanines is discussed below.

We also investigated the isomer distribution of several 2(3)-substituted alkoxyphthalocyanines which are formed under the reaction conditions described above. From earlier work,[6] we already know that a statistical distribution of isomeric 2(3)-tetraalkoxyphthalocyaninatonickel compounds, such as $(C_8H_{17}O)_4$PcNi and $(c\text{-}C_6H_{11}O)_4$PcNi (D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5), was observed starting from the corresponding phthalonitriles and $NiCl_2$ in dimethylaminoethanol. Similar to the formation of **5** and **6** (Scheme 2), we assume a template effect. However, the amount of the D_{2h} isomer of the 2(3)-substituted nickel phthalocyanines, such as $(C_8H_{17}O)_4$PcNi and $(c\text{-}C_6H_{11}O)_4$PcNi, is much higher than that of the 1(4)-substituted phthalocyanines **5** and **6**. During the synthesis of 2(3)-substituted nickel phthalocyanines no steric hindrance takes place when the phthalodinitrile units approach the central metal to form the template, even if this leads to a D_{2h} symmetry (Figure 1).

For the synthesis of a metal-free 2(3)-substituted phthalocyanine under the influence of an alkoxide anion, 1,2-dicyano-4-pentoxybenzene (**4**) was treated with lithium in pentan-1-ol to give 2(3)-tetra-(pentoxy)phthalocyanine (**8**) (Scheme 1). The work up was carried out as described for the metal-free 1(4)-substituted phthalocyanine **7** and led to an almost statistical distribution of the separated isomers (Table 1). In this case the formation of the C_{4h} isomer was not preferred. There are no significant differences in the electron density between the two cyano groups in 4-(2-ethylhexyloxy)-1,2-dicyanobenzene (**9**) (Figure 3). The nucleophilic attack of pentan-1-ol to form the dipolar precursors therefore has no preferred direction and the formation of **8** takes place according to statistical rules.

To further investigate the influence of substituents and their positions on the isomer distribution, we synthesized for the first time 1(4)- and 2(3)-alkoxyphthalocyanines substituted not only with racemic, but with chiral, enantiomerically pure alkoxy groups. It was therefore necessary to prepare both the racemic and the chiral phthalonitrile precursors. For this purpose, 2-phenylbutanol, which can be easily derived from commercially available *R*,*S*-2-phenylbutyric acid, and the pure (+)-*S* and (−)-*R* counterparts were chosen. The corresponding substituted phthalonitriles **10** (racemic, *R* and *S*



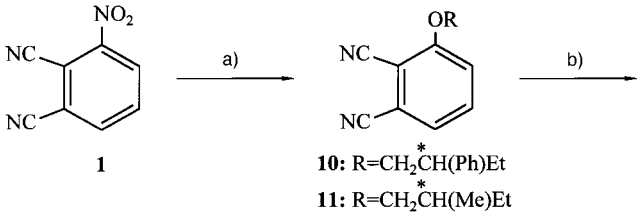
Scheme 2. Synthesis of 1(4)-substituted phthalocyanines. Compounds **5** and **6** are obtained as a mixture of isomers.

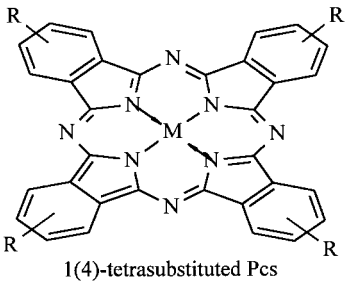
forms) were then prepared by nucleophilic substitution of the nitro group in **1** with the appropriate optically active alcohols (Scheme 3). Reaction of (*R,S*)-, (*S*)-, and (*R*)-**10** with $NiCl_2$ in dimethylaminoethanol for 24 h at 140 °C afforded the desired phthalocyaninatonickel compounds, 1(4)-tetra-(*R,S*-2-phenylbutoxy)phthalocyaninatonickel [(*R,S*)-**13**], 1(4)-tetra-(*S*-2-phenylbutoxy)phthalocyaninatonickel [(*S*)-**13**], and 1(4)-tetra-(*R*-2-phenylbutoxy)phthalocyaninatonickel [(*R*)-**13**] (Scheme 3). By using HPLC to determine the distribution of the four structural isomers in these systems, the following phenomenon was observed: under identical reaction conditions, the nickel phthalocyanines (*S*)-**13** and (*R*)-**13** on the one hand and the racemic nickel phthalocyanine (*R,S*)-**13** on the other hand are again formed with different compositions of their structural isomers (Table 2). The racemic (*R,S*)-**13** shows

Table 2. Isomer distribution in the formation of racemic and optically active 1(4)- and 2(3)-tetrasubstituted nickel phthalocyanines.

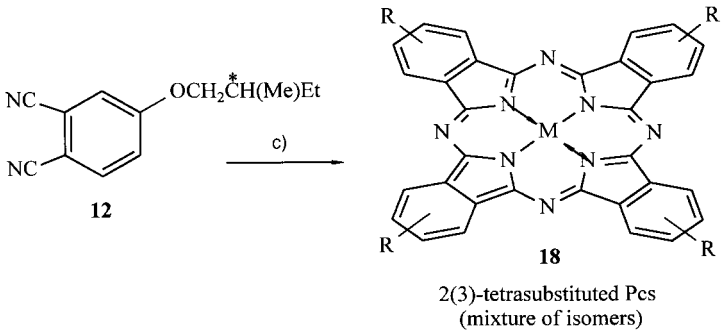
Phthalonitrile	Reaction conditions	Product	Isomer ratio [%][a]			
			D_{2h}	C_S	C_{2v}	C_{4h}
(*R,S*)-**10**	$NiCl_2$/DMAE, 24 h/140 °C	(*R,S*)-**13**	2	57	27	14
(*S*)-**10**	$NiCl_2$/DMAE, 24 h/140 °C	(*S*)-**13**	2.5	50.5	26	21
(*R*)-**10**	$NiCl_2$/DMAE, 24 h/140 °C	(*R*)-**13**	3	49	25	23
(*R,S*)-**12**	$NiCl_2$/DMAE, 6 h/140 °C	(*R,S*)-**18**	10	77		13
(*S*)-**12**	$NiCl_2$/DMAE, 6 h/140 °C	(*S*)-**18**	9	76		15

[a] Statistical distribution; $D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5$.





Compound	M	OR
13	Ni	1(4)-OCH$_2$*CH(Ph)Et
14	Ni	1(4)-OCH$_2$*CH(Me)Et
15	Cu	1(4)-OCH$_2$*CH(Me)Et
16	Zn	1(4)-OCH$_2$*CH(Me)Et
17	H_2	1(4)-OCH$_2$*CH(Me)Et



Scheme 3. Synthesis of 1(4)-substituted phthalocyanines. a) ROH/DMF, K_2CO_3; b) for **13**–**16**: MX_2 (M = Ni, Cu, Zn; X = Cl or OAc)/DMAE, reflux; for **17**: 1) Li/DMAE, reflux; 2) H_2O; c) $NiCl_2$/DMAE, reflux.

the expected distribution of the four structural isomers analogous to the described phthalocyanines **5** and **6** which were formed under comparable conditions. However, in comparison to (*R,S*)-**13** (14 %) the amount of the C_{4h} isomer in the phthalocyanines (*S*)-**13** and (*R*)-**13** increases to 21 and 23 % respectively. The increase of the C_{4h} isomer in (*S*)-**13** and (*R*)-**13** results mainly in a decrease of the C_s isomer (Table 2). Although (*R,S*)-, (*S*)-, and (*R*)-**13** are formed under identical conditions and a template effect can be taken as a basis for all of these reactions, the chiral substituents in (*S*)- and (*R*)-**13** have a pronounced influence on the formation of the respective structural isomers, particularly of the one with the highest symmetry (C_{4h}).

This trend in the distribution of the structural isomers is not found in the formation of 2(3)-substituted phthalocyanines. *R,S*- and *S*-1,2-dicyano-4-(2-methylbutoxy)benzenes [(*R,S*)- and (*S*)-**12**] react with $NiCl_2$ in dimethylaminoethanol for 6 h at 140 °C to give 2,3-tetra-(*R,S*-2-methylbutoxy)phthalocyaninatonickel [(*R,S*)-**18**] and the corresponding (*S*)-**18** (Scheme 3). The isomer ratios are given in Table 2 but the effect observed in the case of the 1(4)-substituted phthalocyanines **13** (and **14**–**17**, see below) is not found in the 2(3)-substituted phthalocyanines **18**. Chiral alkoxy groups in 2(3) position do not change the isomer distribution so that phthalocyanines (*R,S*)- and (*S*)-**18** consist of the usual percentages of isomers according to a statistical synthesis.

The results show that a chiral alkoxy substituent has a directing effect during the formation of the 1(4)-alkoxy-substituted phthalocyaninatonickel system **13** (also for **14**–**17**, see below) favoring the formation of the C_{4h} isomer, but only in the case of 1(4)-alkoxy-substituted phthalocyanines.

At this stage, a more detailed investigation on this anomaly between the optically active and racemic substituents on the formation of 1(4)-substituted phthalocyanines was carried out. For this purpose, we restricted ourselves to 1(4)-substitution, and several 1(4)-tetra-(2-methylbutoxy)phthalocyanines **14**–**17** (Scheme 3) were prepared. The corresponding precursor phthalonitriles (*R,S*)- and (*S*)-**11** were synthesized as described for **2** (see Scheme 1) by treating the commercially available 2-methylbutanol (*S* and *RS*) with the nitrophthalonitrile **1** in good yields (Scheme 3). For the investigations on chiral compounds we restricted ourselves

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to the *S* isomer of 3-(2-methylbutoxy)-1,2-dicyanobenzene [(*S*)-**11**].

The next step was to exchange the central metals under the mentioned identical reaction conditions. For this purpose, (*R*,*S*)- and (*S*)-1,2-dicyano-3-(2-methylbutoxy)benzenes [(*R*,*S*)- and (*S*)-**11**] were treated with the corresponding metal salts $NiCl_2$, $CuCl_2$, and $ZnCl_2$, respectively, in dimethylaminoethanol for 6 h at 140 °C (Scheme 3) to yield 1(4)-tetra-(*R*,*S*-2-methylbutoxy)phthalocyaninatonickel [(*R*,*S*)-**14**], 1(4)-tetra-(*R*,*S*-2-methylbutoxy)phthalocyaninatocopper [(*R*,*S*)-**15**)], 1(4)-tetra-(*R*,*S*-2-methylbutoxy)phthalocyaninatozinc [(*R*,*S*)-**16**], and the corresponding systems (*S*)-**14**, (*S*)-**15**, and (*S*)-**16** with chiral substituents. Additionally, (*R*,*S*)- and (*S*)-1,2-dicyano-3-(2-methylbutoxy)benzenes [(*R*,*S*)- and (*S*)-**11**] were heated without a metal salt in dimethylaminoethanol for 6 h at 140 °C to yield the metal-free 1(4)-tetra-(*R*,*S*-2-methylbutoxy)phthalocyanine [(*R*,*S*)-**17**] and (*S*)-**17**. The distributions of the HPLC separated isomers are given in Table 3 and show that the chiral and racemic OR substituents

Table 3. Influence of central metals on the isomer distribution of 1(4)-tetrasubstituted metal phthalocyanines.

Phthalonitrile	Reaction conditions	Product	Isomer ratio [%][a]			
			D_{2h}	C_S	C_{2v}	C_{4h}
(*R*,*S*)-**11**	$NiCl_2$/DMAE, 6 h/140 °C	(*R*,*S*)-**14**	3	66	21	10
(*S*)-**11**	$NiCl_2$/DMAE, 6 h/140 °C	(*S*)-**14**	2	45	24	29
(*R*,*S*)-**11**	$CuCl_2$/DMAE, 24 h/140 °C	(*R*,*S*)-**15**	2	51	32	15
(*S*)-**11**	$CuCl_2$/DMAE, 6 h/140 °C	(*S*)-**15**	2	45	32	21
(*R*,*S*)-**11**	zinc acetate/DMAE, 6 h/140 °C	(*R*,*S*)-**16**	2	56	30	12
(*S*)-**11**	zinc acetate/DMAE, 6 h/140 °C	(*S*)-**16**	2	52	35	11
(*R*,*S*)-**11**	DMAE, 6 h/140 °C	(*R*,*S*)-**17**	2	45	32	21
(*S*)-**11**	DMAE,6 h/140 °C	(*S*)-**17**	1	47	33	19

[a] Statistical distribution; D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5.

in **10** and **11** not only leads to different distribution of the structural isomers but that this effect also depends on the metal used for the preparation of the metal phthalocyanines. In the case of nickel, the amount of C_{4h} isomer in (*S*)-**14** (29 %) increases clearly in comparison to the racemic counterpart (*R*,*S*)-**14** (10 %) as already seen in the substituted phthalocyanines **13** (Table 3). This difference also appears to a lesser extent in the copper complexes (*R*,*S*)-**15** (15 %) and (*S*)-**15** (21 %), respectively, but is absent in the zinc phthalocyanine (*R*,*S*)/(*S*)-**16** (12/11 %) and in the metal-free phthalocyanines (*R*,*S*) and (*S*)-**17** (21/19 %). The effect runs parallel to the ability of the respective metals to form templates[11] in the reaction of the phthalonitriles **10** and **11** with the respective metal ions. Ni^{2+}, with incomplete d orbitals and its preference for a square-planar coordination geometry is the most suitable and common template cation, particularly for nitrogen-donor macrocycles. Cu^{2+} and Zn^{2+} are less suitable for this kind of molecular recognition. During the synthesis of the metal-free (*R*,*S*)- and (*S*)-**17**, the mechanism shown in Scheme 2 (no template effect) is operative.

Having demonstrated the effects of substituents and central metal atom on the formation of 1(4)-tetrasubstituted phthalocyanines, we investigated the influence of the reaction conditions on the increase of the C_{4h} isomer of the chiral 1(4)-tetra-(*S*-2-methylbutoxy)phthalocyaninatonickel [(*S*)-**14**]. Nickel phthalocyanines (*R*,*S*)-**14** and (*S*)-**14** were prepared from (*R*,*S*)- and (*S*)-1,2-dicyano-3-(2-methylbutoxy)benzenes [(*R*,*S*)- and (*S*)-**11**] first in dimethylaminoethanol, but adding an excess of urea at 140 °C for 6 h. In a second experiment, the reaction was carried out in the same solvent, but in the absence of urea, and finally without solvent in a melt at 140 °C for 6 h. All three reactions were worked up in the same way and led to the results shown in Table 4. The yield of the C_{4h} isomer (*S*)-**14** increased most in the third experiment [(*R*,*S*)-**14**/(*S*)-**14** = 19:48], whereas with addition of urea, this effect disappeared [(*R*,*S*)-14/(*S*)-**14** = 8:9] (Table 4). An explanation for this phenomenon can be found when we consider that the reaction must enforce a template effect to obtain an increase of the C_{4h} isomer of (*S*)-**14**. When urea was used, most probably urea is first coordinated to the metal ion and then gradually exchanged by a phthalodinitrile. The template effect is therefore not valid during the synthesis of (*S*)-**14** in the presence of urea. On the other hand, in a solid-state reaction (melt) without solvent and other reagents, the respective dinitrile units can complex with the metal ion immediately to induce a template effect.

Table 4. Influence of reaction conditions on the isomer distribution of 1(4)-tetrasubstituted nickel phthalocyanines.

Phthalonitrile	Reaction conditions	Product	Isomer ratio[%][a]			
			D_{2h}	C_S	C_{2v}	C_{4h}
(*R*,*S*)-**11**	$NiCl_2$/DMAE/urea, 6 h/140 °C	(*R*,*S*)-**14**	3	46	43	8
(*S*)-**11**	$NiCl_2$/DMAE/urea, 6 h/140 °C	(*S*)-**14**	2	49	40	9
(*R*,*S*)-**11**	$NiCl_2$/DMAE, 6 h/140 °C	(*R*,*S*)-**14**	3	66	21	10
(*S*)-**11**	$NiCl_2$/DMAE, 6 h/140 °C	(*S*)-**14**	2	45	24	29
(*R*,*S*)-**11**	$NiCl_2$/melt, 6 h/140 °C	(*R*,*S*)-**14**	3	47	31	19
(*S*)-**11**	$NiCl_2$/melt, 6 h/140 °C	(*S*)-**14**	1	30	21	48

[a] Statistical distribution; D_{2h}:C_s:C_{2v}:C_{4h} = 12.5:50:25:12.5.

In summary, we have observed a difference between the behavior of 1(4)-alkoxy-substituted phthalocyaninatonickel systems with chiral alkoxy groups (*S*)- and (*R*)-**13** and (*S*)-**14** and the analogous systems substituted with racemic alkoxy groups, (*R*,*S*)-**13** and **14** (Table 2). Investigations of the influence of central metals (Table 3) and reaction conditions (Table 4) show that for those cases in which we can assume a template effect as a basis for these reactions, the proportion of C_{4h} isomer in the chiral systems (*S*)-**13**/(*R*)-**13** and (*S*)-**14** increases significantly in comparison to the values for racemic compounds (*R*,*S*-**13** and **14**).

To understand this observation, model compounds were subjected to semiempirical calculations. They showed no increase in thermodynamic stability in the case of the C_{4h} isomer substituted with chiral alkoxy groups, compared to the C_{4h} isomer substituted with racemic alkoxy groups. No unusual energetic destabilization took place when two neighboring substituents with the same configurations were contacted. All isomers, except the C_{4h} isomer, have at least two of these interacting alkoxy chains (Scheme 2).

If we look at the described phenomenon from a statistical point of view, the isomer distribution found in the case of the phthalocyanines substituted with chiral alkoxy groups can be explained based on the observed statistical composition of the

respective racemic phthalocyanine isomers in the following way: a racemic isomer, for example (*R*,*S*)-**14** (Scheme 3) can be formed either from four molecules of phthalonitriles, for example **10** with *R* or *S* configuration (*RRRR* or *SSSS*) or from a mixture of four molecules of *R*- and *S*-configurated phthalonitriles. The phthalocyanine macrocycle can thus be formed from one *R* and three *S* molecules of phthalonitrile or from two *R* and two *S* molecules of phthalonitriles etc. The lower the symmetry of the respective isomers, the more possibilities exist to compose the isomers from *R*- and *S*-phthalonitrile units (e.g. in the case of (*R*,*S*)-**13**: for the C_{4h} isomer: *RRRR*, *SSSS*, *RSSS*, *SRRR*, *RRSS*, *RSRS*; for the D_{2h} isomer: *RRRR*, *SSSS*, *RSSS*, *SRRR*, *RRSS*, *RSRS*, *SRRS*; for the C_{2v} isomer: *RRRR*, *SSSS*, *RRRS*, *SSSR*, *SRRR*, *RSSS*, *RRSS*, *SSRR*, *RSRS*, *SRRS*; for the C_s isomer: *RRRR*, *SSSS*, *RRRS*, *SSRR*, *RRSR*, *SSRS*, *RSRR*, *SRSS*, *SRRR*, *RSSS*, *RRSS*, *SSRR*, *RSSR*, *SRRS*, *RSRS*, *SRSR*).

The chiral *S*- and *R*-phthalocyanines, for example (*S*)- and (*R*)-**13** consist only of the either *RRRR*- or *SSSS*-phthalonitrile units. As a result of this, the amount of the C_{4h} isomer decreases to a lesser extent than the other three isomers C_s, C_{2v}, and D_{2h}. Thus, the absolute proportion of the four isomers shows an increased amount of the C_{4h} isomer [(*S*)-**13**/(*R*)-**13**, (*S*)-**14**] and a strongly decreased percentage of the C_s isomer.

Experimental Section

General: All reactions were carried out under dry nitrogen and all solvents were dried according to standard methods. Commercially available reagents were used as purchased. NMR spectra were recorded with a Bruker ARX 250, IR spectra with a Bruker IFS 48, mass spectra with a Varian MAT 711, UV/VIS spectra with a Shimadzu UV-365 and UV-3102 PC, elemental analysis with a Carlo Erba Elemental Analyser 1106 and HPLC with Beckmann System Gold (Autosampler 507, Programmable Solvent Module 126 and Diode Array Detector Modu1e 168) and Kronlab system (Mastercron 4 High Performance Pump, Dynamax Absorbance Detector Module UV-1 and Gilson Fraction Collector Model 201).

1,2-Dicyanonitrobenzene and the substituted 1,2-dicyanobenzenes were synthesized according reported procedures.[13–15] 1(4)Tetra-(2-ethylhexyloxy)phthalocyaninatonickel (**5**) was prepared by literature methods.[7]
All reported UV/Vis, ^{1}H NMR, ^{13}C NMR, MS data, and elemental analyses for 1(4)- and 2(3)-substituted phthalocyanines refer to the mixture of structural isomers. The UV/Vis spectra of the pure isomers differ from the UV/Vis spectra of the isomer mixture only in the halfwidth of the bands.

(*R*,*S*)-1,2-Dicyano-3-(2-ethylhexyloxy)benzene [(*R*,*S*)-2]: Anhydrous K_2CO_3 (7.9 g, 0.058 mol) was added to a solution of 1,2-dicyano-3-nitrobenzene (4 g, 0.23 mol) in anhydrous DMF (50 mL) under nitrogen. The mixture was stirred for 30 min at room temperature and then treated with 2-ethylhexanol (9.3 mL, 0.072 mol). After stirring the mixture for two days at 40 °C it was cooled, poured into water, and extracted with toluene. The combined organic extracts were dried with Na_2SO_4 and evaporated. The residue was purified by column chromatography on silica gel (eluent: Et_2O/toluene, 1:1). Yield: 2.9 g (49 %), pale yellow waxy solid, m.p. 80 – 83 °C. Elemental analysis calcd for $C_{16}H_{20}N_2O$ (256.4): C 74.97, H 7.86, N 10.93; found C 75.28, H 8.16, N 10.99; MS (EI): *m*/*z* (%): 256.7 ([M^+], 8), 156.9 (3), 144.0 (16), 112.1 (11), 82.9 (7), 71.0 (85), 57.0 (100), 43.0 (50); IR (KBr disk): $\tilde{\nu}$ = 3088 (w), 2961 (vs), 2930 (vs), 2872 (vs), 2859 (vs), 2232 (m, C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.60 (m, 1H), 7.20 – 7.28 (m, 2H), 3.97 (d, 2H, J = 5.5 Hz), 1.71 (q, 1H, J = 6.1 Hz), 1.34 – 1.54 (m, 4H), 1.18 – 1.27 (m, 4H), 0.79 – 0.90 (m, 6H); ^{13}C NMR ($CDCl_3$): δ = 161.61, 134.55, 124.78, 116.83, 116.76, 115.36, 112.94, 104.67, 72.23, 39.01, 30.14, 28.85, 23.48, 22.79, 10.95.

(*R*,*S*)-, (*S*)- and (*R*)-1,2-Dicyano-3-(2-phenylbutoxy)benzene [(*R*,*S*)-10, (*S*)-10 and (*R*)-10]: 1,2-Dicyano-3-nitrobenzene (3 g, 18 mmol) was stirred with the appropriate (*R*,*S*)-, (*S*)- and (*R*)-2-phenylbutanol (5.2 g, 35 mmol) and anhydrous K_2CO_3 (6 g) in anhydrous DMF (40 mL) at 40 °C for one week. The mixture was poured into ice – water and extracted with toluene. The combined organic phases were dried with Na_2SO_4, the solvent evaporated, and the products purified by column chromatography on silica gel (eluent: toluene/Et_2O, 5:1). Yield: 993 mg (20 %) for (*R*,*S*)-**10**, 1.14 g (23 %) for (*S*)-**10**, and 893 mg (18 %) for (*R*)-**10**; white solid; m.p. 76 – 79 °C. (*S*)-(+)-**12**: $[\alpha]_D^{25}$ = +11 (c = 1, toluene). (*R*)-(−)-**10**: $[\alpha]_D^{25}$ = −10 (c = 1, toluene).

(*R*,*S*)-10: MS (EI): *m*/*z*: 276.2 ([M^+]), 147.1 ([$M^+ - C_2H_5$]); IR (KBr): $\tilde{\nu}$ = 3082, 3030, 2962, 2929, 2873, 2229, 1583, 1475, 1454, 1249, 1051, 800, 762, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS): δ = 7.60 (t, 1H, H-a′), 7.36 (m, 6H, H-1′,2′,3′, H-a or H-b′), 7.19 (d, 1H, H-a or H-b′), 4.24 (m, 2H, H-1), 3.06 (m, 1H, H-2), 1.85 (m), 2.11 (m) (2H, H-3), 0.93 (t, 3H, h-4); ^{13}C NMR ($CDCl_3$/TMS): δ = 161.7 (C-b), 141.3 (C-4′), 134.3 (C-a′), 129.9/128.5 (C-1′, 2′), 127.5 (C-3′), 125.4 (C-b′), 117.4 (C-C′), 117.1 (C-a), 115.2/113.7 (C-d, C-d′), 105.0 (C-C), 74.4 (C-1), 47.5 (C-2), 25.1 (C-3), 12.5 (C-4).

(*R*,*S*)- and (*S*)-1,2-Dicyano-3(2-methylbutoxy)benzene [(*R*,*S*)- and (*S*)-11]: (*R*,*S*)- and (*S*)-**11** were prepared by treating (*R*,*S*)- and (*S*)-2-methylbutanol with 1,2-dicyano-3-nitrobenzene in DMF in the presence of anhydrous K_2CO_3 as described for the preparation of (*R*,*S*)-**2**.

(*R*,*S*)-11: (*R*,*S*)-2-methylbutanol (3.8 g, 43.3 mol), 1,2-dicyano-3-nitrobenzene (3 g, 17.3 mmol), and K_2CO_3 (6.2 g, 44.9 mol) were allowed to react in DMF (30 mL) to give 1.3 g (35 %) of a white solid, m.p. 114 – 116 °C. MS (EI): *m*/z (%): 214 ([M^+], 6), 157.2 (4), 144.2 (80), 127.1 (2), 115.9 (40), 99.9 (15), 89.0 (9), 71.0 (100), 55.1 (12), 43.0 (90); IR (KBr disk): $\tilde{\nu}$ = 3084 (s), 2964 (s), 2936 (vs), 2878 (s), 2237 (s, C≡N), 1581 (vs), 1474 (vs), 1450 (s), 1400 (m), 1381 (m), 1306 (vs), 1288 (vs), 1242 (m), 1178 (m), 1051 (vs), 993 (w), 924 (w), 901 (w), 795 (vs), 729 (w) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.60 (m, 1H), 7.19 – 7.28 (m, 2H), 3.89 (m, 2H), 1.88 (m, 1H), 1.25, 1.52 (m, 2H), 1.00 (d, 3H, J = 6.8 Hz), 0.92 (t, 2H, J = 7.4 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 161.56, 134.56, 124.90, 116.81, 115.36, 112.96, 104.73, 74.48, 34.39, 25.76, 16.25, 11.17.

(*S*)-11: (*S*)-2-Methylbutanol (1.7 g, 19.3 mol), 1,2-dicyano-3-nitrobenzene (3 g, 17.3 mmol), and K_2CO_3 (6.2 g, 44.9 mmol) were allowed to react in DMF (40 mL) to give 1.15 g (31 %) of a white solid; m.p. 113 – 116 °C, $[\alpha]_D^{20}$ = 9.2 (c = 1, toluene); elemental analysis calcd for $C_{13}H_{14}N_2O$ (214.1): C 72.86, H 6.59, N 13.08; found C 72.56, H 7.14, N 13.11.

1(4)-Tetra-(2-ethylhexyloxy)phthalocyaninatocopper (6): A solution of 1,2-dicyano-3-(2-ethylheyloxy)benzene (**1**) (racemate) (0.5 g, 1.9 mmol) in dimethylaminoethanol (10 mL) was heated with $CuSO_4 \cdot 5H_2O$ (120 mg, 0.5 mmol) for 6 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected, and purified by column chromatography (neutral alumina, eluent: $CHCl_3$). Yield 70 mg (13 %) as a blue-green powder. Separation of the isomers by HPLC with (*o*-nitrophenyl)-quinoline-modified silica gel;[6] eluent 70 % toluene and 30 % *n*-hexane; flow 1.5 mL min^{-1}. MS (FD)*: m/z*: 1087.4 ([M^+]), 2176.8 ([M^+])$_2$, 3264.4 ([M^+])$_3$; IR (KBr disk): $\tilde{\nu}$ = 3064 (w), 2957 (vs), 2925 (vs), 2856 (s), 1591 (s), 1489 (m), 1458 (m), 1377 (m), 1338 (s), 1271 (s), 1246 (s), 1177 (w), 1124 (w), 1082 (s), 1064 (s), 941 (w), 887 (w), 796 (w), 756 (w), 740 (s) cm^{-1}; UV ($CHCl_3$): λ = 709, 678, 635, 406, 345, 317, 260 nm; elemental analysis calcd for $C_{64}H_{80}N_8O_4Cu$: C 70.55, H 7.41, N 10.29; found: C 71.00, H 8.10, N 10.62.

1(4)-Tetra-(2-ethylhexyloxy)phthalocyanine (7): Lithium (540 mg, 78 mmol) was heated (100 °C) in 2-ethylhexanol (20 mL) until all of the metal was dissolved. 1,2-dicyano-3-(2-ethylhexyloxy)benzene (**2**) (racemate) (2 g, 4 mmol) was added and heated for 3 h (130 °C). The solvent was removed by distilling under vacuo and the green product was dissolved in chloroform and washed with water. The organic layers were dried over $MgSO_4$. The solvent was evaporated and the product was purified by column chromatography (neutral alumina, eluent: $CHCl_3$). Yield: 847 mg (43 %) as a blue-green powder. Separation of the isomers by HPLC with Machery-Nagel, ET 250/8/4 Nucleosil $5NO_2$; eluent 50 % toluene and 50 % *n*-hexane; flow 1 mL min^{-1}. MS (FD)*: m/z*: 1027 ([M^+]), 2054.4 ([M^+])$_2$, 3264.4 ([M^+])$_3$; ^{1}H NMR (C_6D_6, 250 MHz) signals of the C_{4h} isomer: δ = 9.22 (d, 4H), 8.03 (m, 4H), 7.37 (d, 4H), 4.35-4.47 (m, 8H), 2.49-0.96 (m, 60H), −1.20 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ = 155.71, 149.80, 139.61, 130.60, 123.44, 115.42, 112.33, 76.85/71.82, 40.11/39.29, 30.66, 29.41/29.14, 23.98, 23.32, 14.26/1405, 11.34/11.00; IR (KBr disk): $\tilde{\nu}$ 3062 (w), 2954 (s), 2856 (s), 1587 (m), 1494 (m), 1462 (m); 1454 (m), 1377 (w); 1334 (s), 1309 (m), 1267 (vs), 1224 (w), 1141 (w), 1058 (s); 1012 (s), 925 (w), 869 (w),

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864 (w), 796 (w), 758 (m), 705 (w), 615 (w) cm^{-1}; UV ($CHCl_3$): $\lambda = 723$, 690, 658, 624, 353, 319 nm; elemental analysis calcd for $C_{64}H_{82}N_8O_4$: C 74.82, H 8.05, N 10.91; found C 74.80, H 9.06, N 9.94.

2(3)-Tetra(pentyloxy)phthalocyanine (8): 1,2-dicyano-4-(pentyloxy)benzene (500 mg, 2.35 mmol) was added to a hot solution of lithium (300 mg, 43 mmol) in pentanol (35 mL) and heated for 3 h (130 °C). Workup and purification were carried out as described for **6**; column chromatography (silica gel, eluent: $CHCl_3$). Yield: 237 mg (47 %) as a blue powder. Separation of the isomers by HPLC with (*p*-butyldinitrophenyl)quinoline-modified silica gel;[6] eluent 25% THF and 75% *n*-hexane; flow 1.5 mL min^{-1}. MS (FD): *m/z*: 858.2 ([M^+]); ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 8.29$ (br, 4H), 7.75 (br, 4H), 7.16 (br, 4H), 4.28 (br, 8H), 2.14 (br, 8H), 1.75 (br, 16H), 1.2 (br, 12H), −4.31 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.89 MHz): $\delta = 159.70$, 146.87, 145.79, 136.20, 127.83, 122.16, 117.79, 103.59, 68.07, 29.35, 28.51, 22.82, 14.25; IR (KBr disk): $\tilde{\nu} = 3423$ (w), 2958 (m), 2925 (s), 2854 (m), 1612 (s), 1502 (w), 1485 (w), 1467 (m), 1427 (w), 1386 (m), 1344 (m), 1323 (m), 1261 (vs), 1240 (s), 1097 (vs), 1053 (s), 1018 (s), 850 (w), 804 (s), 752 (m) cm^{-1}; UV ($CHCl_3$): $\lambda = 705$, 668, 647, 607, 344, 300 nm; elemental analysis calcd for $C_{52}H_{58}N_8O_4$: C 72.73, H 6.76, N 13.05; found C 72.21, H 6.55, N 13.84.

1(4)-Tetra-(*R,S*-, *S*-, and *R*-2-phenylbutoxy)phthalocyaninatonickel [(*R,S*)-, (*S*)-, and (*R*)-13]: A solution of 1,2-dicyano-3-(*R,S*-, *S*-, and *R*-2-phenylbutoxy)benzene (0.5 g, 1.8 mmol) in dimethylaminoethanol (10 mL) was heated with $NiCl_2$ (115 mg, 1.4 mmol) for 24 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected and purified by column chromatography (silica gel, eluent: $CHCl_3$). Yield: 115 mg (22 %) for (*R,S*)- and (*R*)-**13**, 94 mg (18 %) for (*S*)-**7**. Separation of the isomers by HPLC with (o-nitrophenyl)quinoline-modified silica gel;[6] eluent 85% toluene and 15% *n*-hexane; flow 1.5 mL min^{-1}. MS (FD): *m/z*: 1162.1 ([M^+]); ^{1}H NMR ($CDCl_3$, 250 MHz): (*R,S*)-**13**: δ = [8.95 (d), 8.72 (d), 8.69 (d), 8.06 (m), 7.83 (m), 7.47 (m), 6.99 (m), 6.96 (m), 6.56 (m), 6.23 (m), 5.99 (m)] 32H, [5.28–5.10 (m), 4.3 (m), 4.15 (m), 3.66 (m), 3.31 (m)] 8H, [2.77 (m), 2.59 (m), 1.93 (m), 1.27 (m), 1.06 (m), 0.63 (m)] 24H; (*S*)- and (*R*)-**13**: δ = [8.99 (d), 8.80 (d), 8.66 (d), 8.22 (m), 7.88 (m), 7.65 (m), 6.94 (m), 6.55 (m), 6.32 (m), 6.01 (m)] 32H, [5.31 (m), 5.01 (m), 4.44 (m), 4.26 (m), 3.65 (m), 3.40 (m)] 8H, [2.82 (m), 2.60-2.57 (m), 1.99–1.90 (m), 1.18 (m), 1.09 (m), 1.01 (m) 0.75 (m)] 24H; ^{13}C NMR ($CDCl_3$, 62.89 MHz): (*R,S*), (*S*)-, and (*R*)-**13**: $\delta = 156.31$–153.91, 145.11, 143.02–142.13, 140.87–138.02, 129.57, 128.9, 127.02, 123.49/122.00, 117.4/116.57, 114.46–133.44, 111.32, 73.23/72.23, 48.54/47.58, 26.31, 12.51; IR (KBr disk): $\tilde{\nu} = 3516$ (m), 2954 (m), 2923 (s), 2852 (m), 1641 (m), 1595 (vs), 1529 (m), 1492 (s), 1483 (s), 1452 (s), 1431 (s), 1377 (w), 1330 (vs), 1263 (vs), 1244 (s), 1197 (m), 1128 (s), 1083 (s), 740 (w); UV ($CHCl_3$) λ 697, 670, 627, 400, 336, 299 nm; elemental analysis calcd for $C_{72}H_{64}N_8O_4Ni$: C 73.61, H 5.98, N 8.61; found C 72.78, H 6.52, N 8.58.

1(4)-Tetra-(*R,S*- and *S*-2-methylbutoxy)phthalocyaninatonickel [(*R,S*)- and (*S*)-14]: A solution of 1,2-dicyano-3-(*R,S* and *S*-2-methylbutoxy)benzene (0.5 g, 2.4 mmol) in dimethylaminoethanol (10 mL) was heated with $NiCl_2$ (115 mg, 1.4 mmol) for 6 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected and purified by column chromatography (neutral alumina, eluent: $CHCl_3$). Yield: 128 mg (28 %) for (*R,S*)-**14**, 260 mg (48 %) for (*S*)-**14.** Separation of the isomers by HPLC with (*o*-nitrophenyl)quinoline-modified silica gel;[6] eluent 90% toluene and 10% *n*-hexane; flow 1 mL min^{-1}. MS (FD): *m/z*: 914.4 ([M^+]); 1828.1 ([M^+]$_2$); ^{1}H NMR (C_6D_6, 250 MHz): (*R,S*)-**14**: δ = [9.37 (d), 9.30 (d), 9.20 (d), 8.82 (d)] 4H, [8.10–7.95 (m), 7.77 (d), 7.67 (d), 7.39 (d), 7.09 (d), 6.99 (d), 6.79 (d), 6.68 (d)] 8H, [5.15–5.06 (m), 4.91–4.82 (m), 4.16–4.10 (m), 3.89 (m), 3.74 (m)] 8H, [2.71–2.68 (m), 2.40-2.09 (m), 1.67–0.97 (m)] 36H; (*S*)-**14**: δ = [9.25–9.15 (m), 8.94 (d), 8.50 (d)] 4H, [8.18–7.94 (m), 7.86–7.66 (m), 7.65–7.57 (m), 7.48 (d), 7.10–7.00 (m), 6.94 (d), 6.78 (d), 6.45 (d), 6.29 (d)] 8H, [5.17–5.07 (m), 4.96–4.86 (m), 4.06–3.96 (m), 3.63 (m), 3.39 (m)] 8H, [2.75 (m), 2.29–1.11 (m)] 36H; ^{13}C NMR ($CDCl_3$, 62.89 MHz): (*R,S*)-**14**: δ = 156.09-153.74, 144.6, 140.35–137.49, 128.66, 125.93–121.64, 115.33, 113.62–109.62, 76.91/73.00, 34.79, 29.69/26.24, 16.34, 11.39; (*S*)-**14**: δ = 156.09–153.99, 144.46, 140.41–137.76, 128.92, 125.93–121.88, 115.42, 113.74–109.89, 76.86/73.36, 34.99, 29.69/26.44, 16.37, 11.41; IR (KBr disk): $\tilde{\nu} = 3070$ (s), 2956 (vs), 2925 (vs), 2871 (vs), 2856 (vs), 1597 (m), 1490 (m), 1462 (m), 1377 (w), 1332 (s), 1273 (vs), 1234 (s), 1176 (w), 1126 (m), 1085 (s), 1062 (s), 952 (m), 898 (w), 794 (w), 758 (w), 740 (m) cm^{-1}; UV ($CHCl_3$): $\lambda = 699$, 671, 628, 400, 375, 335, 298 nm; elemental analysis calcd for $C_{52}H_{56}N_8O_4Ni$: C 68.24, H 6.17, N 12.25; found C 68.29, H 6.49, N 12.16.

1(4)-Tetra-(*R,S*- and *S*-2-methylbutoxy)phthalocyaninatocopper [(*R,S*)- and (*S*)-15]: A solution of 1,2-dicyano-3-(*R,S*- and *S*-2-methylbutoxy)benzene (0.5 g, 2.4 mmol) in dimethylaminoethanol (10 mL) was heated with $CuCl_2$ (188 mg, 1.4 mmol) for 6 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected, and purified by column chromatography (neutral alumina, eluent: $CHCl_3$). Yield: 137 mg (25 %) for (*R,S*)-**15**, 121 mg (22 %) for (*S*)-**15.** Separation of the isomers by HPLC with (*p*-butylnitrophenyl)quinoline-modified silica;[6] eluent 75% n-hexane and 25% THF; flow 1.5 mL min^{-1}. MS (FD): *m/z*: 918.9 ([M^+]); IR (KBr disk): $\tilde{\nu} = 3060$ (m), 2949 (s), 2925 (vs), 2854 (s), 1584 (m), 1489 (m), 1377 (w), 1341 (s), 1268 (vs), 1177 (w), 1124 (w), 1082 (s), 1064 (s), 941 (m), 891 (w), 740 (s) cm^{-1}; UV ($CHCl_3$): $\lambda = 708$, 676, 635, 345, 318, 259 nm; elemental analysis calcd for $C_{52}H_{56}N_8O_4Cu$: C 67.85, H 6.09, N 12.18; found C 67.60, H 6.11, N 11.94.

1(4)-Tetra-(*R,S*- and *S*-2-methylbutoxy)phthalocyaninatozinc [(*R,S*)- and (*S*)-16]: A solution of 1,2-dicyano-3-(*R,S* and *S* 2-methylbutoxy)benzene (0.5 g, 2.4 mmol) in dimethylaminoethanol (10mL) was heated with zinc acetate (307 mg, 1.4 mmol) for 6 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected, and purified by column chromatography (silica gel, eluent: toluene/ether 2:1). Yield: 126 mg (23 %) for (*R,S*)-**16**, 104 mg (19 %) for (*S*)-**16.** Separation of the isomers by HPLC with (*o*-nitrophenyl)quinoline-modified silica;[6] eluent 60% *n*-hexane and 40% THF; flow 1.5 mL min^{-1}. MS (FD): *m/z*: 919.8 ([M^+]); ^{1}H NMR ($CDCl_3$, 250 MHz): (*R,S*)- and (*S*)-**16**: δ = [8.57 (d), 8.46 (d), 7.84 (m), 7.55 (m), 7.12 (m), 6.67 (m), 6.23 (m), 6.08 (m)] 12H, [4.83 (m), 4.78 (m), 3.95 (m), 3.50 (m), 3.19 (m)] 8H, [2.39 (m), 2.21 (m), 2.14 (m), 1.44–0,94 (m)] 36H; ^{13}C NMR ($CDCl_3$, 62.89 MHz): (*R,S*)- and (*S*)-**16**: $\delta = 156.25$–154.59, 152.25, 141.74–138.43, 129.73, 126.35, 117.03, 113.59–112.37, 77.68, 35.44, 26.84, 16.93, 11.73; IR (KBr disk): $\tilde{\nu} = 3440$ (w), 2958 (m), 2925 (m), 2873 (m), 1587 (m), 1488 (s), 1463 (m), 1377 (w), 1336 (vs), 1269 (vs), 1230 (vs), 1174 (m), 1120 (s), 1082 (vs), 1064 (vs), 945 (m), 798 (m), 761 (w), 740 (m) cm^{-1}; UV ($CHCl_3$): $\lambda = 695$, 666, 627, 372, 319 nm; elemental analysis calcd for $C_{52}H_{56}N_8O_4Zn$: C 67.68, H 6.07, N 12.15; found C 65.09, H 6.03, N 11.87.

1(4)-Tetra-(*R,S*- and *S*-2-methylbutoxy)phthalocyanine [(*R,S*)- and (*S*)-17]: A solution of 1,2-dicyano-3-(*R,S*- and *S*-2-methylbutoxy)benzene (0.5 g, 2.4 mmol) in dimethylaminoethanol (10 mL) was heated for 6 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected and purified by column chromatography (silica gel, eluent: $CHCl_3$). Yield: 51 mg (10 %) for (*R,S*)-**17**, 77 mg (15 %) for (*S*)-**17.** Separation of the isomers by HPLC with Machery-Nagel, ET 250/8/4 Nucleosil 5NO_2; eluent 73% *n*-hexane and 27% THF; flow 1.5 mL min^{-1}. MS (FD): *m/z*: 858.1 ([M^+]); ^{1}H NMR ($CDCl_3$, 250 MHz): (*R,S*)- and (*S*)-**17**: δ = [8.99 (m), 8.65 (m), 8.44 (m), 8.06 (m), 7.93 (m), 7.85 (m), 7.66 (m), 7.39 (m), 7.11 (m), 7.01 (m)] 12H, [4.97 (m), 4.77 (m), 4.36 (m), 4.16 (m), 3.97 (m)] 8H, [2.52 (m), 2.32 (m), 1.69 (m), 1.48 (m), 1.33 (m), 1.16 (m), 0.95 (m)] 36H, [−1.01 (s), −1.11 (s), −1.24 (s)] 2H; ^{13}C NMR ($CDCl_3$, 62.89 MHz): (*R,S*)- and (*S*)-**17**: $\delta = 157.03$, 149.74, 140.07, 130.93, 125.11, 116.15, 111.93, 73.92, 35.54/35.3, 26.34, 16.89, 11.73; IR (KBr disk): $\tilde{\nu} = 3438$ (m), 2956 (m), 2923 (s), 2854 (m), 1742 (w), 1589 (s), 1494 (s), 1461 (s), 1377 (m), 1334 (s), 1265 (s), 1224 (s), 1110 (vs), 1089 (vs), 1060 (vs), 1012 (vs), 931 (m), 873 (m), 798 (w), 744 (s) cm^{-1}; UV ($CHCl_3$): $\lambda = 729$, 695, 663, 629, 317 nm; elemental analysis calcd for $C_{52}H_{58}N_8O_4$: C 72.64, H 6.75, N 13.04; found C 71.85, H 7.21, N 11.78.

2(3)-Tetra-(*R,S*- and *S*-2-methylbutoxy)phthalocyaninatonickel [(*R,S*)- and (*S*)-18]: A solution of 1,2-dicyano-3-(R,S and S-2-methylbutoxy)benzene (0.5 g, 2.4 mmol) in dimethylaminoethanol (10 mL) was heated with $NiCl_2$ (115 mg, 1.4 mmol) for 6 h at 140 °C. The crude product was precipitated by adding a methanol/water mixture (1:1), collected, and purified by column chromatography (silica gel, eluent: toluene/ether 1:1). Yield: 192 mg (35 %) for (*R,S*)-**18**, 224 mg (41 %) for (*S*)-**18.** Separation of the isomers by HPLC with (*p*-butylnitrophenyl)quinoline-modified silica gel;[6] eluent 80% n-hexane and 20% THF; flow 1 mL min^{-1}. MS (FD): *m/z*: 914.4 ([M^+]); ^{1}H NMR ($CDCl_3$, 250 MHz): (*R,S*)- and (*S*)-**18**: δ = [7.70–7.45 (m), 7.21–6.87 (m), 6.51–6.39 (m)] 12H, 3.98–3.62 (m) 8H, [1.97 (m), 1.76 (m), 1.40 (m), 1.17 (m)] 36H; ^{13}C NMR ($CDCl_3$, 62.89 MHz): (*R,S*)- and (*S*)-**18**: $\delta = 159.19$, 142.26, 135.91/134.20, 128.86–126.89, 120.89/119.86, 116.93, 101.62, 72.69, 34.87, 26.34, 16.73, 11.59; IR (KBr disk): $\tilde{\nu} = 2958$ (m), 2923 (m), 2873 (w), 1610 (s), 1531 (m), 1483 (m),

1463 (vs), 1388 (w), 1336 (m), 1274 (m), 1238 (vs), 1122 (vs), 1093 (vs), 1066 (s), 950 (w), 740 (m) cm^{-1}; UV ($CHCl_3$): $\lambda = 671$, 639, 605, 379, 328 nm; elemental analysis calcd for $C_{52}H_{56}N_8O_4Ni$: C 68.24, H 6.17, N 12.25; found C 67.87, H 5.87, N 12.81.

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