Synthesis of Crowned Triazolephthalocyanines

Beatriz Cabezón,[a] Ernesto Quesada,[a] Sagrario Esperanza,[a] and Tomás Torres*[a]

Keywords: Phthalocyanines / Triazole macrocycles / Noncentrosymmetric compounds / Crown ether compounds / Aggregation properties

The synthesis of triazolephthalocyanines bearing crown ether and aza-crown ether substituents is described. Different substituents have been introduced on the nitrogen atom of the aza-crown moiety to improve the solubility and the intrinsic amphiphilic character of these macrocycles. The crowned triazolephthalocyanines described have been prepared by a statistical procedure, and also by different variations of a stepwise method. Preliminary studies of the aggregation properties of one representative of this new family of compounds have also been carried out. An exhaustive study of the synthesis of the corresponding dicyano derivative precursors of the triazolephthalocyanines is displayed. Two different approaches have been used for this goal: The first one inserts the cyano groups prior to the synthesis of the crown ether moiety, while the second one builds the crown ether part of the molecule in advance of the cyanation process. The incompatibility of the Rosemund-von-Braun cyanation conditions and the presence of nitrogen atoms in the molecule is the main difficulty of the synthesis of these precursors.

Introduction

Noncentrosymmetrical phthalocyanines[1−4] and related compounds[5,6] have attracted a great deal of attention due to their unusual second-order nonlinear optical properties.[7−9] The special characteristics of these compounds make them suitable for applications as molecular organic materials, for example in opto-electronics.[8] However, the selective synthesis of these systems by classical statistical cyclotretamerization employing two differently substituted phthalonitriles is not easy, especially considering the difficulties in restraining a thermodynamically controlled reaction such as the synthesis of the phthalocyanine macrocycle. Most of the synthetic effort has focused on the preparation of unsymmetrically substituted phthalocyanines with different groups at the periphery of the aromatic system.[10−12] Another approach, which is less developed, involves the preparation of noncentrosymmetrical phthalocyanine analogues, formally obtained by the substitution of one isoindole subunit in a phthalocyanine by another conjugated heterocyclic moiety.[4,13]

As a consequence of our interest in the synthesis of noncentrosymmetrical phthalocyanines with high second-order nonlinear optical responses, we prepared, for the first time, the so-called "triazolephthalocyanine" (Tpc),[14] a phthalocyanine analogue in which one 1,2,4-triazole subunit has formally replaced an isoindole subunit of the phthalocyanine core. These unsymmetrical macrocycles display important second- and third-order nonlinear optical properties in solution,[15] and high thermal stability,[16] similar and even higher to those shown by phthalocyanines. Triazolephthalocyanines bearing peripheral lipophilic substituents have shown liquid-crystal behaviour.[17] Moreover, these compounds can be self-assembled by the Langmuir−Blodgett technique, to afford in-plane organised films[18,19] with semiconducting properties, and can be applied as gas-sensor devices.[20]

Two synthetic methodologies have been developed for obtaining Tpcs: a single-step metal template method, and a two-step method.[21,22] The former, in which the corresponding 1,3-diiminoisoindoline and the 3,5-diamino-1,2,4-triazole (guanazole) are allowed to react in a 3:1 molar ratio in the presence of a metal salt, which acts as template, allows for the preparation of Tpcs bearing the same substituents in the three isoindole moieties.[21] The latter represents a good strategy for the preparation of unsymmetrically substituted Tpcs.[22,23]

A wide variety of triazolephthalocyanines differing in the number and type of substituents have been characterised, but to the best of our knowledge, no examples of crown ethers containing triazolephthalocyanines have been described. On the contrary, crowned Pcs have been extensively studied.[24−31] The introduction of crown ethers in the periphery of the Tpc will be of great interest because of the strong and selective capability of complexation of these moieties that would improve the applications of these macrocycles as molecular materials. As an example, depending on the size of the cation complexed in the crown ether it is possible to control the stacking degree of the macrocycles.[32] Nevertheless, the synthesis of the appropriate 1,2-dicyanobenzene precursors is not obvious, due to the limited synthetic approaches available for introducing cyano subunits on a benzene ring, and the incompatibilities between functional groups.

In the present paper, we describe for the first time, the synthesis of triazolephthalocyanines bearing crown ether substituents that could allow the application of these systems as ion-electronic devices.[28] The introduction of aza-

[a] Organic Chemistry Department (C−I), Autónoma University of Madrid Cantoblanco
28049 Madrid, Spain
Fax: (internat.) + 34-91/397-3966
E-mail: tomas.torres@uam.es

crown substituents is especially suitable, since it allows the introduction of long aliphatic chains in the crown through its nitrogen atom, thus improving the intrinsic amphiphilic character of the Tpcs and supporting their organisation in Langmuir−Blodgett films.[18,19] Preliminary studies of their aggregation properties in solution have also been performed.

Results and Discussion

Bekarouglu and co-workers have previously described aza-crown-substituted phthalocyanine derivatives.[33−35] However, the synthetic route described for preparing the corresponding dicyanobenzene precursors is not convergent enough to allow the introduction of a wide variety of substituents on the amino function of the aza-crown at an advanced step of the synthesis. In an attempt to develop a more versatile procedure for the preparation of *N*-substituted aza-crown derivatives, two different approaches for obtaining 1,2-dicyanobenzo-aza-crown derivatives were studied. The first one introduces the cyano groups prior to the crown ether synthesis (Scheme 1), while the second one builds the crown ether moiety in advance of the cyanation process (Scheme 2). Both procedures employ 4,5-dibromo-catechol (1)[36,37] as starting material.
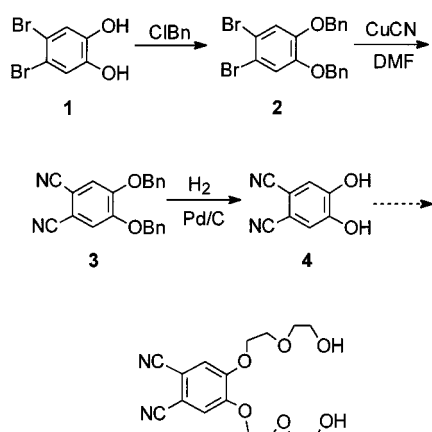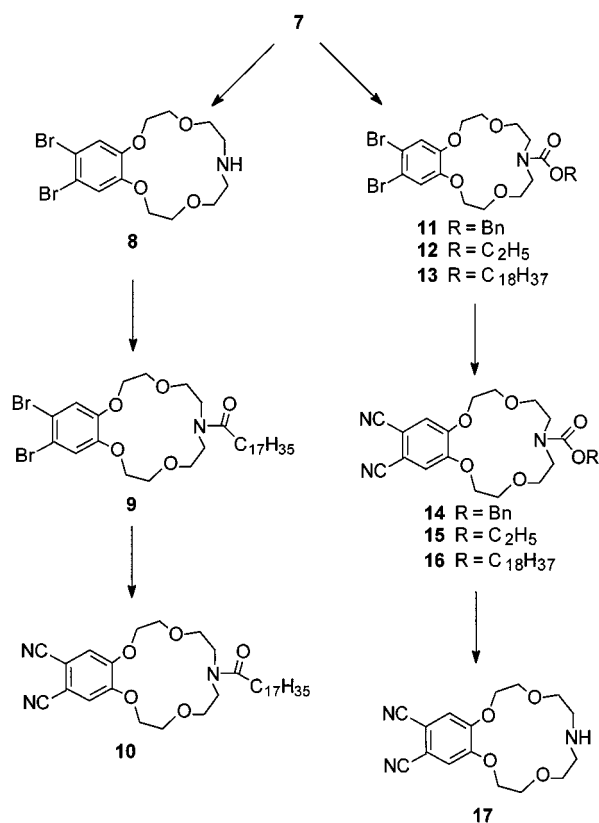

Scheme 1
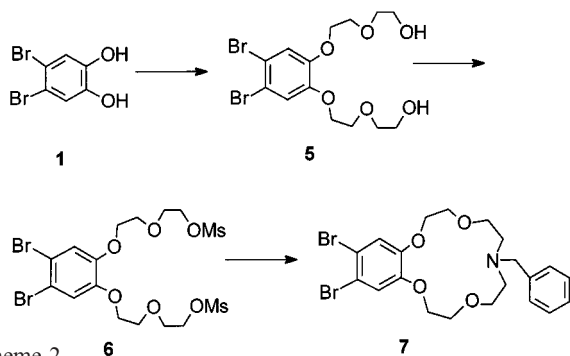
Scheme 2

In the first route (Scheme 1) the key compound is 1,2-dicyanocatechol (4), which has already been prepared by

the Rosenmund-von-Braun reaction starting from 4,5-dibromocatechol (1) conveniently protected as an acetal derivative.[38,39] However, attempts to reproduce the described yields were unsuccessful, probably due to partial cleavage of the acetal under the cyanation conditions. For this reason, a different hydroxy group protection, namely benzylic ethers, was essayed. Thus, 4,5-dibenzyloxy-1,2-dibromobenzene (2) was prepared by reaction of 4,5-dibromocatechol (1) with an excess of benzyl chloride in the presence of potassium carbonate as base. The synthesis of the 4,5-dicyano derivative 3 was carried out by the Rosenmund-von-Braun reaction, with an excess of CuCN in boiling DMF in good yield (60%). The cleavage of the benzylic groups was carried out by hydrogenolysis. Thus, bubbling hydrogen through a suspension of 3, palladium/10% activated carbon, and ethyl acetate afforded 1,2-dicyanocatechol (4) in high yield (91%). However, the alkylation of 4 with 2-(2-chloroethoxy)-ethanol was unsuccessful. Although different solvents, reaction conditions, and alkylating agents were attempted, only traces of monoalkylation and dialkylation products were detected by NMR (estimated yield 5%). The main component of the crude mixture was the starting dicyano derivative 4. The unworkable amounts of dialkylated compound obtained because of the low reactivity of 4 due to the electron-withdrawing effect of the cyano groups eliminated this strategy for preparing dicyanobenzo-aza-crowns.

The second proposed route (Scheme 2) requires the protection of the amino function (NH group of compound 8,[33] Scheme 3), since the high nucleophilic character of the cyanide anions produces undesirable side reactions on this group during further cyanation processes.[33] In this strategy, the key compound is the dibromo compound 7, since it affords the possibility of substituting the benzyl group by a wide variety of carbamate and amide functions (Scheme 2). Compound 7 was prepared in a three-step route. Alkylation of 4,5-dibromocatechol (1) as previously described by Nolte afforded 5.[37] The aza-crown ring closure from 5 required the conversion of the hydroxy functions into an appropriate leaving group, and for this reason, 6 was synthesised in high yield by dropwise addition of a solution of mesyl chloride to a cooled (0 °C) solution of 5. Further condensation of 6 with benzylamine yielded 7.

However, the cyanation of 7 employing the Rosemund-von-Braun conditions did not provide the corresponding dicyano derivative, probably because of the localised electron pair of the secondary amine in the aza-crown subunit, which gives rise to undesired side reactions. In order to overcome this problem, we decided to introduce an electron-delocalising substituent on the aza-crown ether.

To synthesise the dicyanobenzo-aza-crown 10 from 7 (Scheme 3), the cleavage of the benzyl group and the introduction of the amide function before cyanation were necessary. The delocalisation of the electron pair of the nitrogen atom by the amide function enables the cyanation process to proceed in this case. Compound 8, prepared by bubbling hydrogen gas through a suspension of 7 and palladium/10% activated carbon, was allowed to react with stearoyl chloride to provide 9 in high yield. The synthesis of the 4,5-

7

8

11 R = Bn
12 R = C$_2$H$_5$
13 R = C$_{18}$H$_{37}$

9

14 R = Bn
15 R = C$_2$H$_5$
16 R = C$_{18}$H$_{37}$

10

17

Scheme 3

10 X = NCOC$_{17}$H$_{35}$
15 X = NCOOC$_2$H$_5$
16 X = NCOOC$_{18}$H$_{37}$

18 X = O
19 X = NCOC$_{17}$H$_{35}$
20 X = NCOOC$_2$H$_5$
**21** X = NCOOC$_{18}$H$_{37}$

Scheme 4

dicyano derivative **10** was carried out as described above, by the Rosenmund-von-Braun reaction with an excess of CuCN in boiling DMF.

Compounds **11**, **12**, and **13**, bearing a benzyl, ethyl, and octadecyl carbamate moiety, respectively (Scheme 3), were prepared by reaction of **7** in the presence of an excess of the corresponding chloroformate. Again, the cyanation process affords the corresponding dicyano precursors **14**, **15**, and **16** in good yields due to the presence of a carbamate function.

Compounds **14** and **15** are not only precursors to the triazolephthalocyanines described below, but can also be hydrolysed to yield **17**. This versatile compound **17** allows the preparation of dicyanobenzo-aza-crown derivatives with a wide variety of substituents, such as compounds **10** and **16** described above, by reaction with the corresponding acid chloride or chloroformate, respectively. Compound **17** is also especially suitable for preparing dicyanobenzo-aza-crown derivatives alkylated on the amino group that cannot be easily prepared by another way.

1,3-Diiminoisoindolines **18**−**21** (Scheme 4) were prepared following the standard procedure, bubbling ammonia gas through a solution of the corresponding dicyano derivative in dry methanol in the presence of catalytic amounts of sodium methoxide.

To prepare the triazolephthalocyanines, different routes have been employed (Scheme 5). Compound **24** was prepared in a two-step reaction[22] from the three-unit ligand **22a**, which was treated with equimolar amounts of nickel(II) acetate to isolate its mononickel(II) complex **23a** as previously described by us.[40] This complex was then
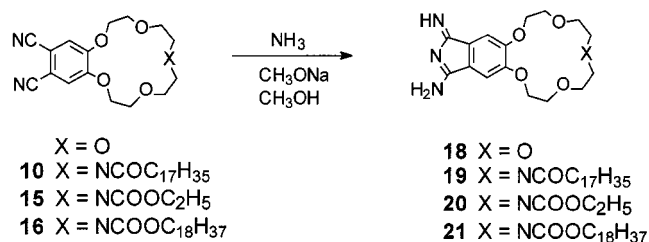
treated (Scheme 5, route a) with equimolar amounts of **18**[41] to afford the triazolephthalocyanine **24**.

To synthesise compound **25**, a two-step one-pot reaction was employed.[22] In this strategy, the three-unit metal complex was prepared in the same way described above, but it was not isolated. The appropriate amount of the 1,3-diiminoisoindoline **20** was added to the reaction mixture produced in the first step, once it had reached the temperature required for the second one (40 °C) (Scheme 5, route b).

Another efficient modification based on this approach was used to prepare **27** and **28** (Scheme 6). The method involves the one-step reaction of equimolar amounts of the three-unit ligands **22a** or **22b**, nickel(II) acetate, and the corresponding 1,3-diiminoisoindoline **21** or **18**, respectively[15] (Scheme 6, route c).

Recently, we have discovered that dicyano derivatives are also able to react with the three-unit ligand **22a** in the presence of the nickel(II) and copper(II) salts to afford the corresponding triazolephthalocyanine employing the same general conditions described above.[42] Triazolephthalocyanine **26** was prepared by this methodology (Scheme 6, route d).

Finally, triazolephthalocyanine **29** (Scheme 7), bearing the same substituents in the three isoindole subunits, was prepared in a very low yield following a statistical procedure. This was done by heating stoichiometric amounts of 5,6-(1,4,7,10,13-pentaoxatridecamethylene)-1,3-diiminoisoindoline (**18**), guanazole, and nickel(II) acetate in 2-ethoxyethanol to reflux (Scheme 7).

Yields of the cyclocondensation reaction mentioned above are relatively lower than those obtained for related alkoxytriazolephthalocyanines.[15,17,19] One reason of this behaviour could be the ease with which crown ethers form aggregates, thereby reducing the reactivity of the 1,3-diiminoisoindoline precursors and also resulting in the difficulties in the purification process. This trend is justified, since the lowest isolated yield corresponds to the triazolephthalocyanine **29** bearing three crown ethers.

All compounds were characterised by elemental analysis, IR, and UV/Vis spectroscopies, mass spectrometry, and NMR techniques.

UV/Vis spectroscopy might be a useful tool for studying aggregation phenomena in phthalocyanines and related compounds in solution.[43] It is well known, that crowned Pcs aggregate in the presence of alkaline metal ions.[24,44]

The electronic absorption spectrum of the monocrown-triazolephthalocyanine **24** in a chloroform/methanol (10:1) solution (ca. 5×10^{-5} M) shows two strong absorption
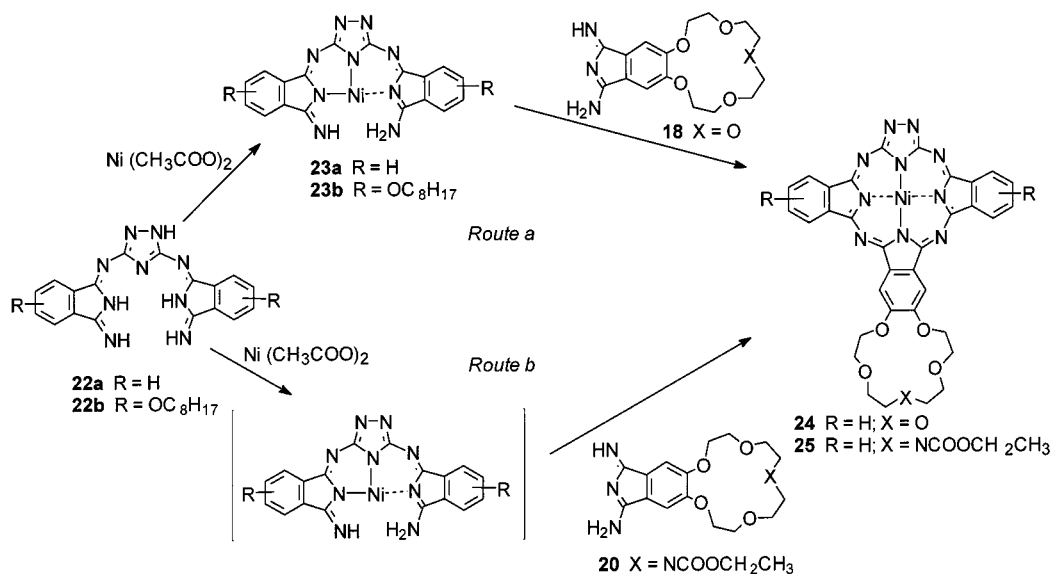
Scheme 5
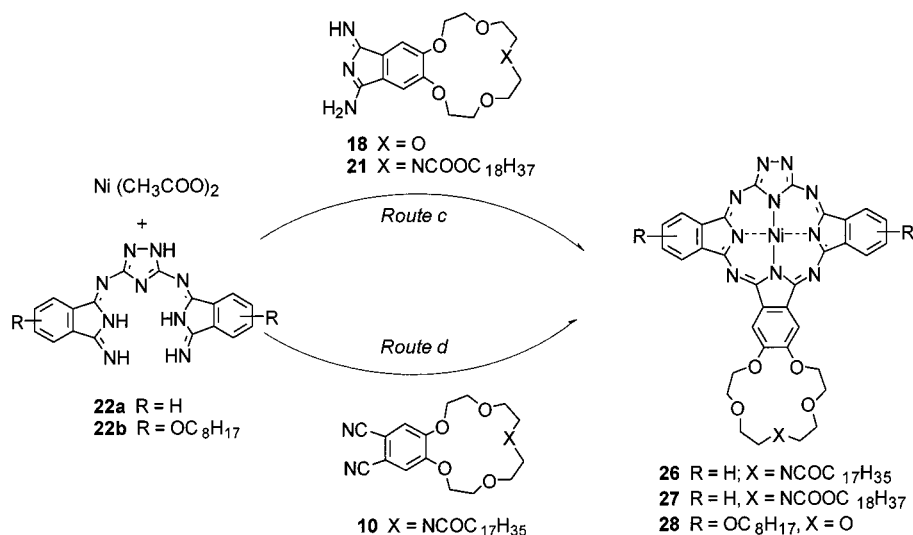
Scheme 6

bands in the near UV region at 260 and 370 nm, together with several weaker absorptions in the UV/Vis region at 525, 570, and 625 nm (Q-band).[14] The addition of potassium acetate to the solution of **24** mentioned above gives rise to notable changes in the UV/Vis spectrum. Spectra were taken at three different molar ratios of macrocycle/salt, namely 1:0.5, 1:1 and 1:10.

On increasing the concentration of the salt, the absorptions corresponding to the bands in the 250−370 nm region increase in intensity, whereas the absorptions corresponding to the bands in the visible region decrease slightly. Similar qualitative results were obtained with a larger ion like Rb^+.

These facts may be rationalised according to our previous experience[43,45] in related compounds, in terms of aggregation of the crowned triazolephthalocyanine indicated by alkali metal ions, which coordinate the crown ether ring. This fact was observed for the first time in triazolephthalocyanine compounds.

Unfortunately, compound **29** bearing three crown ether subunits could not be studied due to its low solubility in chloroform/methanol mixtures. Further studies will be developed with more soluble derivatives related to **29**.

Summary and Conclusion

We have described for the first time, the synthesis of triazolephthalocyanines bearing crown ether and aza-crown subunits. Different substituents have been introduced on the nitrogen atom of the aza-crown moiety to improve the solubility and the intrinsic amphiphilic character of the Tpcs. It will allow us to study the influence of the different functional groups on the organisation properties of the triazolephthalocyanine at a supramolecular level. The crowned triazolephthalocyanines have been prepared, not only by a statistical procedure, but also by different variations of a stepwise method.
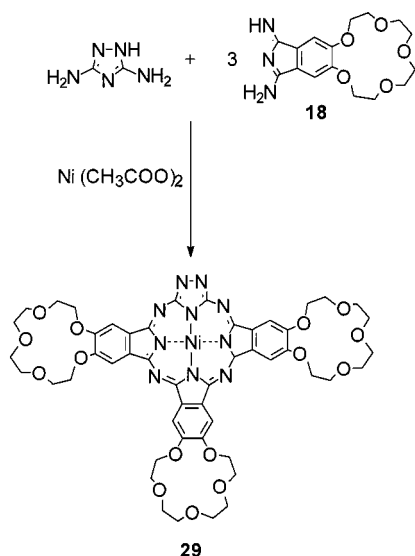
Scheme 7

An exhaustive study of the synthesis of the corresponding dicyano derivative precursors of the triazolephthalocyanines has been carried out. Different routes have been developed and several interesting key compounds (**4**, **7**, and **17**) have been synthesised. Compound **7** is a good target for preparing dicyanobenzo-aza-crown derivatives where the electron pair of the nitrogen atom is delocalised. The incompatibility between the Rosemund-von-Braun cyanation and the presence of nitrogen atoms bearing a localised electron pair makes compound **17** an interesting target for preparing *N*-alkyl-dicyanobenzo-aza-crown derivatives. Unfortunately, the most versatile compound, dicyanocatechol **4**, does not allow for the preparation of this kind of systems due to its low reactivity.

Preliminary aggregation studies carried out on triazolephthalocyanine **24** show the formation of aggregates in solution in the presence of potassium and rubidium salts, with promising results, and will be reported at due course. Studies for preparing films from crowned triazolephthalocyanines based on the Langmuir−Blodgett technology are also being carried out.

Experimental Section

Techniques: UV/Vis and IR spectra were recorded with Perkin−Elmer Model Lambda 6 and PU 9716 Philips spectrometers, respectively. − Melting points were determined with a Büchi melting-point apparatus and are uncorrected. − NMR spectra were recorded with a Bruker WM-200-SY spectrometer with either the solvent as reference or TMS as the internal standard. All chemical shifts are quoted on the δ scale. All coupling constants are expressed in Hertz (Hz). − Fast atom bombardment mass spectra (FAB-MS) were obtained from a VG AutoSpec. Samples of the molecules were dissolved in a small volume of *m*-nitrobenzyl alcohol and loaded on to a stainless steel probe tip. Microanalyses were performed by the Universidad Autónoma de Madrid University Microanalytical Service.

Synthesis: Compounds **1**,[36,37] **4**,[38] **5**,[37] **8**,[33] **18**,[41] and **22**,[17,46] have been previously described. Starting materials were purchased from Aldrich Chemical Co. and used as received without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature.

1,2-Dibenzyloxy-4,5-dibromobenzene (2): A mixture of **1**[36,37] (5.00 g, 18.66 mmol), benzyl chloride (7.10 g, 56.00 mmol), K_2CO_3 (15.50 g, 112.00 mmol), and ethanol (75.0 mL) was stirred under reflux for 8 h. After cooling to room temperature, the solvent was removed and the crude extracted in a mixture water/CH_2Cl_2. The organic solution was dried with anhydrous Na_2SO_4 and the solvent was removed. Washing in methanol afforded 6.5 g of **2**. Yield 78%. M.p. 138−140 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.5−7.3 (m, 10 H, H Ar), 7.17 (s, 2 H, H Ar), 5.11 (s, 4 H, 2·CH$_2$ Bz). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 148.9 (C-1), 136.3 (C-1′), 128.6 (C-3′), 128.1 (C-4′), 127.4 (C-2′), 119.5 (C-2), 115.5 (C-3), 71.7 (CH$_2$ Bz). − EM-EI; *m/z*: 448 [M$^+$], 181. − IR (KBr): ν̃ = 3040, 2930, 2870, 1556, 1490, 1464, 1350, 1240, 1190, 1000, 755, 700 cm^{-1}. − C$_{20}$H$_{16}$Br$_2$O$_2$ (448.1524) : C 53.60, H 3.60; found C 53.52, H 3.41.

1,2-Dibenzyloxy-4,5-dicyanobenzene (3): A mixture of **2** (5.00 g, 11.20 mmol), CuCN (7.00 g, 78.10 mmol), and dry DMF (100 mL) was heated under reflux for 21 h under argon. After cooling to room temperature, ammonium hydroxide was added and air was bubbled through the mixture for 8 h. After filtration of the crude mixture, the residue was purified by recrystallisation in methanol to afford 2.28 g of **3** as a white solid. Yield 60%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.5−7.3 (m, 10 H, H Ar), 7.19 (s, 2 H, H Ar), 5.13 (s, 4 H, CH$_2$ Bz). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 152.8 (C-1), 135.2 (C-1′), 129.6 (C-3′), 129.3 (C-4′), 127.9 (C-2′), 117.9 (C-2), 116.3 (CN), 109.7 (C-3), 72.1 (CH$_2$ Bz). − EM-EI; *m/z*: 340 [M$^+$], 249, 181. − IR (KBr): ν̃ = 3126, 3060, 2940, 2880, 2230 (CN), 1590, 1530, 1360, 1290, 1230, 1080, 960, 885, 705, 692 cm^{-1}. − C$_{22}$H$_{16}$N$_2$O$_2$ (340.3798) : C 77.63, H 4.74, N 8.23; found C 77.03, H 4.91, N: 8.10%.

4,5-Dihydroxyphthalonitrile (4):[38] A solution of **3** (3.40 g, 10.10 mmol) in ethyl acetate (100 mL) was added to a suspension of Pd/10% activated C, 475.00 mg) in ethyl acetate (100 mL). After the addition, hydrogen was bubbled through at room pressure and temperature for 4 h. The crude mixture was filtered through Celite to isolate 1.47 g of compound **4** (recrystallisation from CCl$_4$ or hexane/AcOEt, 3:1). Yield 91%. M.p. > 200 °C (ref.[38] 285 °C). − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.27 (s, 2 H). − ^{1}H NMR ([D$_6$]acetone, 200 MHz): δ = 7.40 (s, 2 H). − ^{1}H NMR ([D$_6$]DMSO, 200 MHz): δ = 7.16 (s, 2 H). − ^{13}C NMR ([D$_6$]DMSO, 50 MHz): δ = 154.7 (C-1), 123.8 (C-2), 120.5 (CN), 109.3 (C-3). − EM-EI; *m/z*: 160 [M$^+$], 114, 100. − IR (KBr): ν̃ = 3500−2600 (OH), 2240 (CN),1610, 1590, 1530, 1450, 1337, 1090, 900, 840 cm^{-1}.

4,5-Dibromo-1,2-bis{2′-[2′′(methylsulfonyloxy)ethoxy]ethoxy}-benzene (6): Mesyl chloride (0.53 g, 4.6 mmol) was added dropwise to a solution of **5**[37] (822 mg, 1.85 mmol), CH$_2$Cl$_2$ (10 mL), and Et$_3$N (840 mg, 8.35 mmol) under stirring at 0° C. After addition, the mixture was stirred for 2 h at 0 °C and then allowed to reach room temperature. The crude was washed with water (50 mL), satd. aq. NaCl (50 mL), 5% HCl (100 mL), satd. aq. NaHCO$_3$ (50 mL), and water (50 mL). The organic phase was dried with anhydrous magnesium sulfate and the solvent removed under reduced pressure to afford **6** (999 mg) as a brown oil that could be used without further purification. Yield 90% (recrystallisation from hexane/Ac-OEt, 7:3). M.p. 50−51 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ =

7.12 (s, 2 H, H Ar), 4.41 (t, 4 H, CH$_2$OMs), 4.16 (t, 4 H, CH$_2$OAr), 3.8−3.9 (m, 8 H, CH$_2$OCH$_2$), 3.09 (s, 6 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 149.2 (C-1), 119.3 (C-2), 116.1 (C-3), 70.2 (CH$_2$OAr), 70.0 (CH$_2$O), 69.9 (CH$_2$OCH$_2$OMs), 38.4 (CH$_3$). − EM-EI; *m/z*: 600 [M$^+$], 293, 167. − C$_{16}$H$_{24}$Br$_2$O$_{10}$S$_2$ (600.2836) : C 32.01, H 4.03, S 10.68; found C 32.34, H 3.85, S 10.86.

1,2-(7-Benzyl-7-aza-1,4,10,13-tetraoxatridecamethylene)-4,5-dibromobenzene (7): A mixture of **6** (12.93 g, 21.54 mmol), benzylamine (2.31 g, 21.54 mmol), Na$_2$CO$_3$ (12.4 g, 120 mmol), and dry acetonitrile (150 mL) was stirred under reflux for 3 d. After cooling to room temperature, the solvent was removed and the crude mixture extracted with a water/CH$_2$Cl$_2$ mixture. The organic solution was dried with anhydrous MgSO$_4$ and the solvent was removed. The crude product was further purified by column chromatography (Al$_2$O$_3$, hexane/AcOEt, 3:1) to afford 5.25 g of **7** as a white solid. Yield 47%. M.p. 100−102 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.4−7.2 (m, 5 H, H Ar), 7.05 (s, 2 H, H Ar), 4.10 (t, 4 H, CH$_2$OAr), 3.86 (t, 4 H, OCH$_2$) 3.70 (t, 4 H, CH$_2$O), 3.67 (s, 2 H, CH$_2$ Bz), 2.81 (t, 4 H, NCH$_2$). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 149.5 (C-1), 140.2 (C-1′), 129.3 (C-2′), 128.7 (C-3′), 127.4 (C-4′), 118.5 (C-2), 115.6 (C-3), 71.5 (CH$_2$OAr), 70.3 (CH$_2$O), 69.6 (OCH$_2$), 61.0 (CH$_2$N), 55.0 (NCH$_2$ Bz). − EM-EI; *m/z*: 515 [M$^+$], 458, 293, 190, 162. − IR (KBr): ṽ = 2880, 2820, 2790, 1580, 1500, 1450, 1350, 1250, 1200, 1135, 1110, 1080, 1040, 850, 740 cm^{-1}. − C$_{21}$H$_{25}$Br$_2$NO$_4$ (515.2392): C 48.95, H 4.89, N 2.72; found C 48.99, H 4.87, N 2.69.

1,2-(7-Aza-1,4,10,13-tetraoxatridecamethylene)-4,5-dibromobenzene (4,5-Dibromobenzomonoaza-15-crown-5) (8):[33] A solution of **7** (2.38 g, 4.62 mmol) in ethyl acetate (25 mL) was added to a suspension of Pd/10% activated C (475 mg) in ethyl acetate (25 mL). After the addition, hydrogen was bubbled through at room pressure and temperature for 48 h. The crude mixture was filtered through Celite and purified by chromatography (Al$_2$O$_3$, AcOEt/MeOH, 10:1) affording 606 mg of compound **8**. Yield 31%. M.p. 143 °C (ref.[33] 142−144 °C). − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.03 (s, 2 H, H Ar), 4.1 (t, 4 H, CH$_2$OAr), 3.86 (t, 4 H, CH$_2$O), 3.73 (t, 4 H, CH$_2$O), 2.84 (t, 4 H, NCH$_2$), 2.30 (br. s, 1 H, NH). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 148.5 (C-1), 116.6 (C-2), 114.5 (C-3), 70.2 (CH$_2$OAr), 68.5 (CH$_2$O), 67.9 (CH$_2$O), 49.0 (NCH$_2$). − IR (KBr): ṽ = 3300, 2950, 2920, 2850, 1570, 1490, 1440, 1350, 1250−1210, 1070, 1040, 960 cm^{-1}. − C$_{14}$H$_{19}$Br$_2$NO$_4$ (425.1148) : C 39.55, H 4.50, N 3.29; found C 39.53, H 4.56, N 3.21.

4,5-Dibromo-1,2-(7-heptadecylcarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)benzene (9): Stearoyl chloride (470 mg, 1.55 mmol) was added to a mixture of **8**[33] (600 mg, 1.41 mmol), Et$_3$N (290 mg, 2.82 mmol), and CH$_2$Cl$_2$ (10 mL) stirred at room temperature. After 8 h, the crude mixture was washed with water (3 × 10 mL) and NaCl successively, and the organic solution was dried with anhydrous MgSO$_4$. The solution was filtered through Al$_2$O$_3$, and the removal of CH$_2$Cl$_2$ gave 810 mg of **9** as a white solid, which was recrystallised from hexane/ethyl acetate. Yield 83%. M.p. 67−68 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.06, 7.05 (2 s, 2 H, H Ar), 4.09 (m, 4 H, ArOCH$_2$), 3.90 (m, 4 H, CH$_2$O), 3.8−3.7 (m, 4 H, OCH$_2$), 3.57 (m, 4 H, CH$_2$N), 2.33 (t, 2 H, NCOCH$_2$), 1.62 (m, 2 H, CH$_2$ β), 1.25 (s, 28 H, CH$_2$), 0.88 (t, 3 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 173.7 (CO), 148.7, 148.7 (C-1), 117.7 (C-2), 115.5, 115.3 (C-3), 71.3, 70.5 (ArOCH$_2$), 70.4, 69.8 (CH$_2$O), 69.1 (OCH$_2$), 50.5, 49.6 (CH$_2$N), 34.7, 33.2, 31.9, 29.7, 29.5, 29.4, 27.6, 25.4, 22.7, 14.1 (CH$_2$). − C$_{32}$H$_{53}$Br$_2$NO$_5$ (691.5804): C 55.58, H 7.72, N 2.03; found C 55.41, H 7.90, N 2.32%.

4,5-Dicyano-1,2-(7-heptadecylcarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)benzene (10): A mixture of **9** (500 mg, 0.72 mmol), CuCN (194 mg, 2.17 mmol), and dry DMF (4.5 mL) was heated to reflux for 18 h under argon. After cooling to room temperature, ammonium hydroxide was added and air was bubbled through the mixture for 8 h. After filtration of the crude mixture, the residue was purified by column chromatography (Al$_2$O$_3$, hexane/AcOEt, 1:1) to afford 63 mg of **10** as a white solid. Yield 15%. M.p. 108−110 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.14, 7.13 (2 s, 2 H, H Ar), 4.18 (m, 4 H, ArOCH$_2$), 3.95 (m, 4 H, CH$_2$O), 3.9−3.7 (m, 4 H, OCH$_2$), 3.6 (m, 4 H, CH$_2$N), 2.4 (t, 2 H, NCOCH$_2$), 1.62 (m, 2 H, CH$_2$ β), 1.25 (s, 28 H, CH$_2$), 0.88 (t, 3 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 173.5 (CO), 152.2, 152.1 (C-1), 115.5 (C-2, CN), 109.1 (C-3), 71.3, 70.5 (ArOCH$_2$), 70.4, 69.8 (CH$_2$O), 69.1, 68.4 (OCH$_2$), 50.4, 49.5 (CH$_2$N), 33.1, 31.9, 29.7, 29.5, 29.3, 25.4, 22.7 (CH$_2$), 14.1 (CH$_3$). − EM-EI; *m/z*: 583 [M$^+$], 540, 359, 318, 289, 260. − C$_{34}$H$_{53}$N$_3$O$_5$ (583.8078): C 69.95, H 9.15, N 7.20; found C 69.60, H 9.18, N 6.86.

1,2-(7-Benzyloxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)-4,5-dibromobenzene (11): A solution of benzyl chloroformate (1.04 g, 6.10 mmol), *N*-benzyldibromo derivative **7** (1.57 g, 3.05 mmol), and dry THF (50 mL) was heated to reflux for 6 h. After extraction with water/CH$_2$Cl$_2$, the organic solution was dried with anhydrous MgSO$_4$ to afford 1.36 g of **11** as a white solid. Yield 80%. M.p. 99−101 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.4−7.3 (m, 5 H, H Ar), 7.05, 7.04 (2 s, 2 H, H Ar), 5.14 (s, 2 H, COOCH$_2$), 4.05 (m, 4 H, ArOCH$_2$), 3.9−3.7 (m, 8 H, CH$_2$OCH$_2$), 3.52 (t, 4 H, CH$_2$N). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 156.0 (CO), 148.6 (C-1), 136.7 (C-1′), 128.5 (C-2′), 127.9 (C-3′), 127.8 (C-4′), 117.4 (C-2), 114.9 (C-3), 70.9, 70.3 (ArOCH$_2$), 69.9, 69.3 (CH$_2$O), 69.3, 69.1 (OCH$_2$), 67.1 (COOCH$_2$), 50.5, 49.8 (CH$_2$N). − EM-EI; *m/z*: 560 [M$^+$], 154, 136, 107. − IR (KBr): ṽ = 3058, 2942, 2872, 2366, 1957, 1698, 1594, 1498, 1475, 1455, 1412, 1370, 1250, 1204, 1157, 1117, 1093, 981, 858, 740, 700 cm^{-1}. − C$_{22}$H$_{25}$Br$_2$NO$_6$ (559.2482): C 47.40, H 4.52, N 2.51; found C 47.58, H 4.75, N 2.57.

4,5-Dibromo-1,2-(7-ethoxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)benzene (12): Ethyl chloroformate (217 mg, 2.00 mmol) was added dropwise to a solution of **7** in dry THF (5 mL) and heated to reflux. After 2 h, the mixture was cooled to room temperature and extracted with water and CH$_2$Cl$_2$. The organic solution was dried with anhydrous MgSO$_4$ and the solvent was removed. The crude mixture was further purified by column chromatography (Al$_2$O$_3$, hexane/AcOEt, 3:1) to afford 415 mg of **12** as a white solid which was recrystallised from AcOEt/hexane. Yield 86%. M.p. 103−104 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.05 (s, 2 H, H Ar), 4.16 (q, 3 H, COOCH$_2$), 4.09 (t, 4 H, ArOCH$_2$), 3.9−3.7 (m, 8 H, CH$_2$OCH$_2$), 3.52 (t, 4 H, CH$_2$N), 1.25 (t, 3 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 156.2 (CO), 148.6 (C-1), 117.4 (C-2), 115.0 (C-3), 70.9, 70.4 (ArOCH$_2$), 69.8, 69.3 (CH$_2$O), 69.3, 69.1 (OCH$_2$), 61.2 (COOCH$_2$), 50.3, 49.6 (CH$_2$N), 14.7 (CH$_3$). − EM-EI; *m/z*: 497 [M$^+$], 466, 418, 381, 293, 186, 158, 114. − C$_{17}$H$_{23}$Br$_2$NO$_6$: C 41.07, H 4.66, N 2.32; found C 41.03, H 4.75, N 2.25.

4,5-Dibromo-1,2-(7-octadecyloxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)benzene (13): A solution of octadecyl chloroformate[47] (960 mg, 2.89 mmol), the *N*-benzyl derivative **7** (1.49 g, 2.89 mmol), and dry THF (40 mL) was heated to reflux for 8 h. After removal of the solvent, the crude mixture was purified by column chromatography (Al$_2$O$_3$, hexane/AcOEt, 3:1) to afford 1.10 g of **13**. Yield 53%. M.p. 64−68 °C. − ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.04 (s, 2 H, H Ar), 4.07 (m, 8 H, ArOCH$_2$,-

COOCH$_2$), 3.9−3.7 (m, 8 H, CH$_2$OCH$_2$), 3.48 (t, 4 H, CH$_2$N), 1.62 (m, 2 H, CH$_2$ β), 1.25 (s, 30 H, CH$_2$), 0.88 (t, 3 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 156.3 (CO), 148.7, 148.7 (C-1), 117.5, 117.5 (C-2), 115.1, 115.0 (C-3), 70.9, 70.5 (ArOCH$_2$), 69.9, 69.3 (CH$_2$O), 69.3, 69.3 (OCH$_2$), 65.5 (COOCH$_2$), 50.3, 49.7 (CH$_2$N), 35.3, 31.9, 29.7, 29.6, 29.3, 29.3, 29.0, 25.9, 22.6 (CH$_2$) 14.1 (CH$_3$). − EM-EI: m/z: 722 [M$^+$], 426, 294, 136, 114.− IR (KBr): ṽ = 2940, 2850, 1693, 1496, 1454, 1410, 1377, 1357, 1350, 1316, 1254, 1203, 1161, 1120, 1056, 981, 860 cm^{-1}. − C$_{33}$H$_{55}$Br$_2$NO$_6$: C 55.06, H 7.71, N 1.95; found C 55.28, H 7.85, N 1.99.

1,2-(7-Benzyloxycarbonyl-7-aza-1,4,10,13-tetraoxatrideca-methylene)-4,5-dicyanobenzene (14): A mixture of **11** (1.36 g, 2.42 mmol), CuCN (694 mg, 7.75 mmol), and dry DMF (20 mL) was heated to reflux for 21 h under argon. After cooling to room temperature, ammonium hydroxide was added and air was bubbled through the mixture for 8 h. After filtration of the crude mixture, the residue was purified by column chromatography (Al$_2$O$_3$, hex-ane/AcOEt, 1:1) to afford 319 mg of **14** as a white solid. Yield 30%. M.p. 164−166 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.4−7.3 (m, 5 H, H Ar), 7.11 and 7.10 (2 s, 2 H, H Ar), 5.14 (s, 2 H, COOCH$_2$), 4.14 (m, 4 H, ArOCH$_2$), 3.9−3.7 (m, 8 H, CH$_2$OCH$_2$), 3.52 (t, 4 H, CH$_2$N). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 156.0 (CO), 152.2 (C-1), 136.7 (C-1′), 128.5 (C-2′), 128.0 (C-3′), 127.8 (C-4′), 115.7 (CN), 115.6 (C-2), 108.9 (C-3), 71.2, 70.5 (ArOCH$_2$), 69.9, 69.6 (CH$_2$O), 68.9, 68.7 (OCH$_2$), 67.1 (COOCH$_2$), 50.5, 49.8 (CH$_2$N). − C$_{23}$H$_{25}$N$_3$O$_6$: C 62.86, H 5.73, N 9.56; found C 62.78, H 6.03, N 9.43.

4,5-Dicyano-1,2-(7-ethoxycarbonyl-7-aza-1,4,10,13-tetraoxatri-decamethylene)benzene (15): A mixture of **12** (1.66 g, 3.34 mmol), CuCN (0.96 g, 10.70 mmol), and dry DMF (35 mL) was heated to reflux for 10 h under argon. After cooling to room temperature, ammonium hydroxide was added and air was bubbled through the mixture for 8 h. After filtration of the crude mixture, the residue was purified by column chromatography (Al$_2$O$_3$, hexane/AcOEt, 1:1) to afford 0.73 g of **15** as a white solid. Yield 56%. M.p. 172−175 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.13 (s, 2 H, H Ar), 4.16 (q, 3 H, COOCH$_2$), 4.15 (t, 4 H, ArOCH$_2$), 3.9−3.7 (m, 8 H, CH$_2$OCH$_2$), 3.49 (t, 4 H, CH$_2$N), 1.25 (t, 3 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 156.2 (CO), 152.2 (C-1), 115.6 (CN), 115.5 (C-2), 108.9 (C-3), 71.1, 70.6 (ArOCH$_2$), 69.9, 69.6 (CH$_2$O), 68.9, 68.6 (OCH$_2$), 61.3 (COOCH$_2$), 50.3, 49.7 (CH$_2$N), 14.7 (CH$_3$). − EM-EI. m/z: 389 [M$^+$], 346, 332, 318, 286, 260, 231, 186, 171. − IR (KBr): ṽ = 3437, 2227, 1698, 1590, 1566, 1523, 1413, 1294, 1160, 1136, 1094, 892 cm^{-1}. − C$_{19}$H$_{23}$N$_3$O$_6$: C 58.60, H 5.95, N 10.79; found C 58.41, H 6.12, N 10.39.

4,5-Dicyano-1,2-(7-octadecyloxycarbonyl-7-aza-1,4,10,13-tetraoxa-tridecamethylene)benzene (16): A mixture of **13** (800 mg, 1.11 mmol), CuCN (298 mg, 3.33 mmol), and dry DMF (12 mL) was heated to reflux for 11 h under argon. After cooling to room temperature, ammonium hydroxide was added and air was bubbled through the mixture for 8 h. After filtration of the crude mixture, the residue was purified by column chromatography (Al$_2$O$_3$, hex-ane/AcOEt, 3:1) to afford 285 mg of **16** as a white solid. Yield 42%. M.p. 116−118 °C. − ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.11, 7.10 (2 s, 2 H, H Ar), 4.16 (t, 4 H, ArOCH$_2$), 4.08 (t, 2 H, COOCH$_2$), 3.92 (dd, 4 H, CH$_2$O), 3.8 (dd, 4 H, OCH$_2$), 3.48 (dd, 4 H, CH$_2$N), 1.62 (m, 2 H, CH$_2$ β), 1.25 (s, 30 H, CH$_2$), 0.88 (t, 3 H, CH$_3$). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 156.3 (CO), 152.3 (C-1), 115.9 (C-2), 115.7 (CN), 108.6 (C-3), 71.2, 70.7 (ArOCH$_2$), 69.9, 69.5 (CH$_2$O), 68.9, 68.6 (OCH$_2$), 65.6 (COOCH$_2$), 50.4, 49.8 (CH$_2$N), 35.3, 31.9, 29.7, 29.6, 29.3, 29.0, 26.0, 22.7 (CH$_2$) 14.1 (CH$_3$). − EM-EI; m/z: 614 [M$^+$], 362, 344, 318, 154, 138, 114, 107. − IR

(KBr): ṽ = 3122, 3051, 2918, 2850, 2228, 1693, 1591, 1524, 1470, 1414, 1366, 1290, 1235, 1165, 1135, 1095, 895 cm^{-1}. − C$_{35}$H$_{55}$N$_3$O$_6$: C 68.47, H 9.04, N: 6.85; found C 68.26, H 8.57, N 6.83.

1,2-(7-Aza-1,4,10,13-tetraoxatridecamethylene)-4,5-dicyanobenzene (4,5-Dicyanobenzomonoaza-15-crown-5) (17). − Method A: Equim-olar amounts of **15** (100 mg, 0.26 mmol) and trimethylsilyl iodide (TMSI), in CHCl$_3$ (3 mL), were heated to reflux under an inert gas. Additional molar amounts of TMSI were added after 6 h and 12 h. After 18 h, MeOH (10 mL) was added and the crude mixture was extracted in water/CH$_2$Cl$_2$. After removal of the organic solvent, the crude mixture was purified by column chromatography (Al$_2$O$_3$, hexane/AcOEt, 1:1 and AcOEt/MeOH, 10:1) to afford 36 mg of **17** as a white solid. Yield 30%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.08 (s, 2 H, H Ar), 4.16 (m, 4 H, ArOCH$_2$), 3.92 (m, 4 H, CH$_2$O), 3.78 (m, 4 H, OCH$_2$), 2.86 (t, 4 H, CH$_2$N), 2.1 (br. s, 1 H, NH). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 152.2 (C-1), 115.8 (CN), 115.2 (C-2), 108.7 (C-3), 70.5 (ArOCH$_2$), 68.3 (CH$_2$O), 68.1 (OCH$_2$), 49.1 (CH$_2$N). − EM-EI; m/z: 318 [M$^+$], 154, 136, 121, 107. − C$_{16}$H$_{11}$N$_3$O$_4$: C 62.14, H 3.58, N 13.59; found C 62.02, H 3.45, N 13.83. − **Method B:** A solution of **14** (43.2 mg, 0.096 mmol) in ethyl acetate (4 mL) was added to a suspension of Pd/10% activated C (475 mg) in ethyl acetate (4 mL). After the ad-dition, hydrogen was bubbled through at room pressure and tem-perature for 12 h. The crude mixture was filtered through Celite and removal of the solvent afforded 28 mg of compound **17**. Yield 80%.

1,3-Diiminoisoindolines 19, 20 and 21. − General Procedure:[48] A solution of the corresponding dicyanobenzo-crown (**10**, **15**, and **16**, respectively) in methanol was treated with ammonia gas in the pres-ence of a catalytic amount of sodium methoxide and heated to reflux for 6−12 h. After filtration of the crude mixture, the solid was washed with NH$_4$Cl to afford the corresponding 1,3-diimin-oisoindoline as a white solid. The compounds were used without further purification in the next reaction step.

5,6-(7-Heptadecylcarbonyl-7-aza-1,4,10,13-tetraaoxatrideca-methylene)-1,3-diiminoisoindoline (19): Yield: 90%. M.p. 150 °C (de-comp.). − ^{1}H NMR ([D$_1$]TFAA, 200 MHz): δ = 7.92 (br. s, 2 H, H Ar), 4.4−4.1 (m, 8 H, ArOCH$_2$CH$_2$), 3.94 (m, 4 H, OCH$_2$), 3.84 (m, 4 H, CH$_2$N), 2.52 (t, 2 H, COOCH$_2$), 1.49 (m, 2 H, CH$_2$ β), 1.23 (br. s, 28 H, CH$_2$), 0.92 (t, 3 H, CH$_3$). − ^{13}C NMR ([D$_1$]TFAA, 50 MHz): δ = 184.3 (CO), 168.9, 168.9 (C-1), 159.5, 158.9 (C-5), 124.9, 124.4 (C-3a), 112.6, 112.5 (C-4), 74.0, 72.6 (Ar-OCH$_2$), 72.4, 72.1 (CH$_2$O), 72.0, 70.2 (OCH$_2$), 56.7, 54.9 (CH$_2$N), 35.2, 34.8, 32.5, 32.5, 32.5, 32.2, 32.0, 31.9, 28.5, 25.3 (CH$_2$), 15.6 (CH$_3$). − IR (KBr): ṽ = 3300−3200, 2930, 2850, 1634, 1600, 1550, 1523, 1464, 1443, 1423, 1292, 1195, 1137, 1059 cm^{-1}.

5,6-(7-Ethoxycarbonyl-7-aza-1,4,10,13-tetraaoxatridecamethylene)-1,3-diiminoisoindoline (20): Yield: 91%. M.p. 180 °C (decomp.). − ^{1}H NMR ([D$_1$]TFAA, 200 MHz): δ = 8.19 (br. s, 2 H, H Ar), 4.58 (m, 2 H, COOCH$_2$), 4.49 (m, 4 H, CH$_2$OAr), 4.39 (m, 4 H, CH$_2$O), 4.19 (m, 4 H, CH$_2$O), 3.9 (m, 4 H, CH$_2$N), 1.42 (t, 3 H, CH$_3$). − ^{13}C NMR ([D$_1$]TFAA, 50 MHz): δ = 163.8 (C-1), 157.3 (CO), 154.6 (C-5), 119.7 (C-4), 108.2 (C-3a), 68.3 (ArOCH$_2$), 67.9 (CH$_2$O), 67.4 (OCH$_2$), 62.7 (CH$_2$N), 47.2 (COOCH$_2$), 11.1 (CH$_3$). − EM-EI; m/z: 407 [M$^+$], 307, 289, 139, 136, 123. − IR (KBr): ṽ = 3250−3125, 2925, 2870, 1702, 1587, 1442, 1413, 1305, 1223, 1130, 1058 cm^{-1}.

1,3-Diimino-5,6-(7-octadecyloxycarbonyl-7-aza-1,4,10,13-tetraoxa-tridecamethylene)isoindoline (21): Yield: 86%. M.p. 150 °C (de-comp.). − ^{1}H NMR ([D$_1$]TFAA, 200 MHz): δ = 8.2 (br. s, 2 H, H

Ar), 4.6−4.4 (m, 6 H, COOCH$_2$, 2·CH$_2$OAr), 4.4 (m, 4 H, CH$_2$O), 4.2 (m, 4 H, CH$_2$O), 3.9 (m, 4 H, CH$_2$N), 1.8 (m, 2 H, CH$_2$ β), 1.5 (br. s, 30 H, CH$_2$), 0.9 (t, 3 H, CH$_3$). − ^{13}C NMR ([D$_1$]TFAA, 50 MHz): δ = 164.3 (C-1), 157.3 (CO), 154.7 (C-5), 119.7 (C-4), 107.7 (C-3a), 68.6 (ArOCH$_2$), 68.0 (CH$_2$O), 62.7 (CH$_2$N), 47.3, 47.1 (COOCH$_2$), 30.1, 27.8, 27.4, 27.3, 26.8, 23.9, 20.6 (CH$_2$), 10.9 (CH$_3$). − IR (KBr): ṽ = 3278, 3231, 2949, 2848, 1702, 1536, 1470, 1435, 1418, 1301, 1217, 1239, 1067, 885 cm^{-1}.

{7,12:21,24-Diimino-5,26:14,19-dinitrilo-9,10-(1,4,7,10,13-pentaoxatridecamethylene)tribenzo[*f,k,p*][1,2,4,9,14,19]hexaazacycloicosinato-(2−)-*N^{27},N^{28},N^{29},N^{30}*}nickel(II) (24): A mixture of the corresponding [3,5-bis(3′-imino-1′-isoindolinylidenamino)-1,2,4-triazolato]-nickel(II) (23a)[40] (73.30 mg, 0.21 mmol), 1,3-diimino-5,6-(1,4,7,10,13-pentaoxatridecamethylene)isoindoline (18) (69.20 mg, 0.21 mmol), and 2-ethoxyethanol (15 mL) was stirred at 50 °C for 3 d. After filtration, the crude mixture was triturated with methanol and the triazolephthalocyanine was extracted with chloroform. Finally, after vacuum evaporation of the solvent, the residue was washed with methanol and filtered to yield 36 mg of 24. Yield: 25%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.4−6.5 (br. signal, 10 H), 3.7−3.5 (m, 8 H, OCH$_2$), 3.5 (s, 8 H, OCH$_2$). − MS-FAB (3-NBA, CDCl$_3$); *m/z*: 713, 715 [M + H$^+$]. − IR (KBr): ṽ = 3600−3200, 2924, 2854 (C−H), 1600, 1500, 1470, 1440 (C=N), 1350, 1290, 1120, 1075, 1050, 760 cm^{-1} (C−H). − UV/Vis (CHCl$_3$): λ (log ε/dm^3 mol^{-1} cm^{-1}) = 259 (4.57), 370 (4.42), 530 (4.00), 628 nm (4.12). − C$_{34}$H$_{26}$N$_{10}$NiO$_5$·H$_2$O: C 55.84, H 3.86, N 19.15; found C 55.58, H 3.71, N 19.21.

{9,10-(7-Ethoxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f,k,p*]-[1,2,4,9,14,19]hexaazacycloicosinato(2−)-*N^{27},N^{28},N^{29},N^{30}*}-nickel(II) (25): A mixture of 3,5-bis(3′-imino-1′-isoindolinylidenamino)-1,2,4-triazole (22a) (0.13 g, 0.37 mmol), and Ni(OAc)$_2$ (93 mg, 0.37 mmol) in 2-ethoxyethanol (10 mL) was heated at 80 °C for 2 h. After cooling to 55 °C, 5,6-(7-ethoxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)-1,3-diiminoisoindoline (20) (0.15 g, 0.37 mmol) in 2-ethoxyethanol (10 mL) was added and the mixture was stirred for 3 d at this temperature. The solid was isolated by filtration and it was treated as described above affording 96 mg of 25. Yield: 29%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.4−6.5 (br. signal, 10 H), 4.5−3.0 (m, 18 H, OCH$_2$), 0.88 (m, 3 H, CH$_3$). − MS-FAB (3-NBA, CDCl$_3$); *m/z*: 784, 786 [M + H$^+$]. − IR (KBr): ṽ = 3600−3000, 2928, 2870 (C−H), 1679 (N−CO−O), 1600, 1500, 1471, 1449 (C=N), 1383, 1352, 1290, 1120, 1069, 754, 725 cm^{-1} (C−H). − UV/Vis (CHCl$_3$): λ (log ε/dm^3 mol^{-1} cm^{-1}) = 259 (4.23), 364 (3.99), 517 (sh), 562 (3.58), 626 nm (3.52). − C$_{37}$H$_{31}$N$_{11}$NiO$_6$·4 H$_2$O: C 51.89, H 4.59, N 17.99; found C 51.51, H 4.35, N 17.88.

{9,10-(7-Heptadecylcarbonyl-7-aza-1,4,10,13-tetrataoxatridecamethylene)-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo-[*f,k,p*][1,2,4,9,14,19]hexaazacycloicosinato(2−)-*N^{27},N^{28},N^{29},N^{30}*}-nickel(II) (26): Equimolar amounts of 3,5-bis(3′-imino-1′-isoindolinylidenamino)-1,2,4-triazole (22a) (59 mg, 0.17 mmol), Ni(OAc)$_2$·4H$_2$O (41 mg, 0.17 mmol), 4,5-dicyano-1,2-(7-heptadecylcarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)benzene (10) (100 mg, 0.17 mmol), and 2-ethoxyethanol (5 mL) were stirred at 50 °C for 3 d. The solid was isolated by filtration and was treated as described above. Further purification by column chromatography (silica gel, CH$_2$Cl$_2$/MeOH, 15:1) was required to yield 43 mg of 26. Yield: 26%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.8−6.5 (br. signal, 10 H), 4.0−3.3 (m, 16 H, OCH$_2$), 2.4 (m, 2 H, NCOCH$_2$), 1.29 (s, 35 H, CH$_2$), 0.92 (m, 3 H, CH$_3$). − MS-FAB (3-NBA, CDCl$_3$); *m/z*: 992, 994 [M + H$^+$].

− IR (KBr): ṽ = 3500−3200, 2921, 2851 (C−H), 1644 (N−CO), 1600, 1500, 1468, 1438 (C=N), 1360, 1289, 1117, 1072, 727 cm^{-1} (C−H). − UV/Vis (CHCl$_3$): λ (log ε/dm^3 mol^{-1} cm^{-1}) = 261 (4.30), 282 (4.30), 371 (4.10), 435 (sh), 530 (3.67), 576 (3.61), 631 nm (3.70). − C$_{53}$H$_{63}$N$_{11}$NiO$_5$·4 H$_2$O: C 59.78, H 6.72, N 14.47; found C 59.48, H 7.19, N: 14.02.

{9,10-(7-Octadecyloxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo-[*f,k,p*][1,2,4,9,14,19]hexaazacycloicosinato(2−)-*N^{27},N^{28},N^{29},N^{30}*}-nickel(II) (27): Equimolar amounts of 3,5-bis(3′-imino-1′-isoindolinylidenamino)-1,2,4-triazole (22a) (41 mg, 0.12 mmol), Ni(OAc)$_2$·4H$_2$O (28.9 mg, 0.12 mmol), 1,3-diimino-5,6-(7-octadecyloxycarbonyl-7-aza-1,4,10,13-tetraoxatridecamethylene)-isoindoline (21) (71 mg, 0.12 mmol), and 2-ethoxyethanol (20 mL) were stirred at 50 °C for 3 d. The solid was isolated by filtration and it was treated as described above. Further purification by column chromatography (silica gel, CH$_2$Cl$_2$/MeOH, 20:1) was required to yield 28 mg of 27. Yield: 24%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.4−6.5 (br. signal, 10 H), 4.5−3.4 (3·m, 18 H, OCH$_2$), 1.29 (m, 32 H, CH$_2$), 0.92 (m, 3 H, CH$_3$). − MS-FAB (3-NBA, CDCl$_3$); *m/z*: 1008, 1010 (M + H$^+$). − IR (KBr), ṽ: 3600−3000, 2922, 2851 (C−H), 1699 (N−CO−O), 1598, 1468, 1413 (C=N), 1351, 1289, 1129, 1067, 772, 754, 723 cm^{-1} (C−H). − UV/Vis (CHCl$_3$): λ (log ε/dm^3 mol^{-1} cm^{-1}) = 260 (4.52), 355 (4.21), 571 (sh), 619 nm (3.54). − C$_{53}$H$_{63}$N$_{11}$NiO$_6$·4 H$_2$O: C 58.89, H 6.62, N 14.25; found C 58.55, H 6.82, N 13.85.

{2(3),16(17)-Dioctyloxy-9,10-(1,4,7,10,13-pentaoxatridecamethylene)-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo-[*f,k,p*][1,2,4,9,14,19]hexaazacycloicosinato(2−)-*N^{27},N^{28},N^{29},N^{30}*}-nickel(II) (28): A mixture of 3,5-bis(3′-imino-5′(6′)-octyloxy-1′-isoindolinylidenamino)-1,2,4-triazole (22b) (0.10 g, 0.16 mmol) and Ni(OAc)$_2$ (41 mg, 0.16 mmol) in 2-ethoxyethanol (20 mL) was heated at 80 °C for 2 h. After cooling to 55 °C, 1,3-diimino-5,6-(1,4,7,10,13-pentaoxatridecamethylene)isoindoline (18) (55 mg, 0.16 mmol) in 2-ethoxyethanol (10 mL) was added and the mixture was stirred for 3 d at this temperature. The solid was isolated by filtration and it was treated as described above. Further purification by column chromatography (silica gel, CH$_2$Cl$_2$/MeOH, 15:1) was required to yield 15 mg of 28. Yield: 10%. M.p. > 200 °C. − ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.6−6.5 (3 m, 8 H), 4.0−3.3 (2 m, 20 H, OCH$_2$), 1.7 (m, 4 H, OCH$_2$CH$_2$), 1.33 (s, 20 H, CH$_2$), 0.92 (t, 6 H, CH$_3$). − MS-FAB (3-NBA, CDCl$_3$); *m/z*: 969, 971 (100) [M + H]$^+$, 857, 855 (24) [M − C$_8$H$_{16}$ + H]. − IR (KBr): ṽ = 3600−3200, 2920, 2850 (C−H), 1610, 1490, 1470, 1440 (C=N), 1370, 1330, 1290, 1245, 1120, 1075, 1040, 830, 765 cm^{-1} (C−H). − UV/Vis (CHCl$_3$): λ (log ε/dm^3 mol^{-1} cm^{-1}) = 279 (4.20), 366 (3.90), 400 (sh), 529 (3.50), 572 (3.40), 637 nm (3.22). − C$_{50}$H$_{58}$N$_{10}$NiO$_5$·3 H$_2$O: C 64.36, H 6.91, N 15.01; found C 64.21, H 7.13, N 14.85.

{7,12:21,24-Diimino-5,26:14,19-dinitrilo-2,3:9,10:16,17-tris-(1,4,7,10,13-pentaoxatridecamethylene)tribenzo[*f,k,p*][1,2,4,9,14,19]-hexaazacycloicosinato(2−)-*N^{27},N^{28},N^{29},N^{30}*}nickel(II) (29): 1,3-Diimino-5,6-(1,4,7,10,13-pentaoxatridecamethylene)isoindoline (18) (0.50 g, 1.49 mmol), 3,5-diamino-1,2,4-triazole (0.05 g, 0.50 mmol), Ni(OAc)$_2$ 4H$_2$O (0.12 g, 0.50 mmol), and 2-ethoxyethanol (20 mL) were stirred under reflux for 48 h. After filtration, the crude material was triturated with methanol and the triazolephthalocyanine was extracted with chloroform. Finally, after vacuum evaporation of the solvent, the residue was washed with hot methanol and filtered to yield 20 mg of 29. Yield: 4%. M.p. > 200 °C. − ^{1}H NMR ([D$_1$]TFAA, 200 MHz): δ = 8.5−7.5 (br. signal, 6 H), 4.8−4.0 (3·m, 48 H, OCH$_2$). − MS-FAB (3-NBA,

TFAA); m/z: 1093, 1095 [M + H$^+$]. − IR (KBr): $\tilde{\nu}$ = 3600−3200, 2920, 2880 (C−H), 1600, 1500, 1485, 1460 (C=N), 1355, 1290, 1120, 1085, 1055, 840, 765 cm^{-1} (C−H). − UV/Vis (CHCl$_3$): λ (log ε/dm^3 mol^{-1} cm^{-1}) = 280 (4.30), 355 (3.85), 430 (sh), 490 (sh), 590 (3.36), 620 nm (3.19). − C$_{50}$H$_{54}$N$_{10}$NiO$_{15}$·4 H$_2$O: C 54.24, H 5.64, N 12.65; found C 53.92, H 5.99, N 12.96.

Acknowledgments

[1] C. C. Leznoff, A. B. P. Lever (Eds), *Phthalocyanines − Properties and Applications*, VCH, Cambridge, **1989**, **1993**, **1996**, *vol. 1−4*.

[2] M. Hanack, H. Heckmann, R. Polley, *Methods Org. Chem. (Houben−Weyl)* **1998**, *vol. E9d*, p. 717.

[3] M. Hanack, M. Hees, P. Stihler, G. Winter, L. R. Subramanian, *Handbook of Conducting Polymers* (Eds.: Skotheim, Elsenbaum, Reynolds), **1997**, p. 381.

[4] G. de la Torre, M. Nicolau, T. Torres, *Supramolecular Photosensitive and Electroactive Materials*, J. Wiley & Sons, Chichester, in press.

[5] M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre, T. Torres, *Synthesis* **1996**, 1139.

[6] F. Fernández-Lázaro, T. Torres, B. Hauschel, M. Hanack, *Chem. Rev.* **1998**, *98*, 563.

[7] G. de la Torre, T. Torres, F. Agulló-López, *Adv. Mater.* **1997**, *9*, 265.

[8] G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, *J. Mater. Chem.* **1998**, *8*, 1671.

[9] B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **1998**, *49*, 12808.

[10] A. Weitmeyer, H. Kliesch, D. Wöhrle, *J. Org. Chem.* **1995**, *60*, 4900.

[11] A. Sastre, B. del Rey, T. Torres, *J. Org. Chem.* **1996**, *61*, 8591.

[12] S. V. Kudrevich, S. Gilbert, J. E. Van Lier, *J. Org. Chem.* **1996**, *61*, 5706.

[13] N. Kobayashi, R. Kondo, S. Nakajima, T. Osa, *J. Am. Chem. Soc.* **1990**, *112*, 9640.

[14] M. Nicolau, B. Cabezón, T. Torres, *Coord. Chem. Rev.* **1999**, *190−192*, 231.

[15] B. Cabezón, G. Rojo, F. Agulló-López, T. Torres, *J. Phys. Chem. A*, in press.

[16] V. Stefani, E. L. G. Denardin, D. Samios, T. Torres, B. Cabezón, *J. Mater. Chem.*, in press.

[17] B. Cabezón, M. Nicolau, J. Barberá, T. Torres, *Chem. Mater.*, in press.

[18] F. Armand, M. V. Martínez-Díaz, B. Cabezón, P. A. Albouy, A. Ruaudel-Teixier, T. Torres, *J. Chem. Soc., Chem. Commun.* **1995**, 1673.

[19] F. Armand, B. Cabezón, M. V. Martínez-Díaz, A. Ruaudel-Teixier, T. Torres, *J. Mater. Chem.* **1997**, *7*, 1741.

[20] F. Armand, O. Araspin, A. Barraud, B. Cabezón, T. Torres, *Synthetic Metals* **1997**, *84,* 879.

[21] A. Sastre, F. Fernández-Lázaro, T. Torres, *J. Chem. Soc., Chem. Commun.* **1994**, 1525.

[22] B. Cabezón, S. Rodríguez-Morgade, T. Torres, *J. Org. Chem.* **1995**, *60*, 1872.

[23] For the preparation of related compounds see: E. V. Kudrik, M. K. Islyaikin, R. P. Smirnov, *Russ. J. Organ. Chem*. **1997**, *33*, 1107.

[24] N. Kobayashi, M. Togashi, T. Osa, K. Ishii, S. Yamauchi, H. Hino, *J. Am. Chem. Soc.* **1996**, *118*, 1073.

[25] H. Engelkamp, S. Middelbeek, R. J. M. Nolte, *Science* **1999**, *284*, 785.

[26] C. F. van Nostrum, S. J. Picken, R. J. M. Nolte, *Angew. Chem.* **1994**, *106*, 2298.

[27] F. Steybe, J. Simon, *New J. Chem.* **1998**, *22*, 1305.

[28] T. Toupance, H. Benoit, D. Sarazin, J, Simon, *J. Am. Chem. Soc.* **1997**, *119*, 9191.

[29] D. Pernin, K. Haberroth, J. Simon, *J. Chem. Soc., Perkin Trans. 1* **1997**, 1265.

[30] M. Kandaz, O. Bekaroglu, *J. Porphyrins Phthalocyanines* **1999**, *3*, 339.

[31] A. R. Oezkaya, A. I. Okur, A. Guel, O. Bekaroglu, *J. Coord. Chem.* **1994**, *33*, 311.

[32] R. Hendriks, O. E. Sielcken, W. Drenth, R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.* **1986**, 1464.

[33] E. Musluoglu, V. Ahsen, A. Gül, Ö. Bekaroglu, *Chem. Ber.* **1991**, *124,* 2531.

[34] E. Musluoglu, V. Ahsen, A. Gül, Ö. Bekaroglu, *Chem. Ber.* **1989**, *122,* 1073.

[35] Z. Z. Öztürk, E. Musluoglu, V. Ahsen, A. Gül, Ö. Bekaroglu, *J. Mater. Sci.* **1992,** *27,* 6283.

[36] M. Kohn, *J. Am. Chem. Soc.* **1951**, *73*, 480.

[37] C. F. Van Nostrum, S. J. Picken, A. J. Schouten, R. J. M. Nolte, *J. Am. Chem. Soc.* **1995**, *117*, 9957.

[38] M. J. Cook, R. Hersons, J. Mc Murdo, D. A. Russell, *J. Mater. Chem.* **1996**, *6*, 149.

[39] Y. Cho, Y. Lim, *Mol. Cryst. Liq. Cryst.* **1988**, *1*, 2107.

[40] S. Rodríguez-Morgade, T. Torres, *Inorg. Chim. Acta* **1995**, *153*, 230.

[41] O. E. Sielken, L. A. Van der Kuil, W. Drenth, J. Schoonman, R. J. M. Nolte, *J. Am. Chem. Soc.* **1990**, *112*, 3086.

[42] B. Cabezón, M. Nicolau, T. Torres, in preparation.

[43] See, for example: J. A. Duro, T. Torres, *Chem. Ber* **1993**, *126*, 269.

[44] T. Toupance, V. Ahsen, J. Simon, *J. Am. Chem. Soc.* **1994**, *116*, 5352.

[45] F. Fernández-Lázaro, A. Sastre, T. Torres, *J. Chem. Soc., Chem. Commun.* **1995**, 419.

[46] F. Fernández-Lázaro, S. Rodríguez-Morgade, T. Torres, *Synthetic Metals* **1994**, *62*, 281.

[47] A. Dembele, H. Deshayes, J. P. Pete, *Bull. Soc. Chim. Fr.* **1988**, 671.

[48] P. J. Brach, S. J. Grammatica, O. A. Ossanna, L. Weinberger, *J. Heterocycl. Chem.* **1970**, 1403.

Received February 11, 2000
[O00062]