

Synthesis, Spectroscopic, and Electrochemical Studies of 1,2-Naphthalene-Ring-Fused Tetraazachlorins, -bacteriochlorins, and -isobacteriochlorins: The Separation and Characterization of Structural Isomers

Elena A. Makarova,^[a] Takamitsu Fukuda,^[b] Evgeny A. Luk'yanets,*^[a] and Nagao Kobayashi*^[b]

Abstract: 1,2-Naphthalene-ring-expanded tetraazachlorins (TACs), tetraazabacteriochlorins (TABCs), and tetraazaisobacteriochlorins (TAiBCs) have been synthesized. Procedures for the synthesis of the starting materials, that is, derivatives of 1,2-naphthalenedicarboxylic acid, have been reinvestigated and improved. Nine possible derivatives, including four, two, and three structural isomers of TACs, TABCs, and TAiBCs, respectively, were separated by using thin-layer chromatography (TLC) or high-performance liquid chromatography (HPLC), and the structure of each isomer was determined by ¹H NMR spectroscopy combined with the NOE technique. The formation ratio of each isomer was rationalized in terms of the intramolecu-

lar steric repulsion effect, which was predicted by geometry optimizations at the DFT level. The derived compounds were characterized by using IR, electronic, and magnetic circular dichroism (MCD) spectroscopy, and by electrochemical methods. Frequency calculations at the DFT level correctly reproduced the experimental IR spectra and, in particular, distinguished between the three isomers of the TAiBCs. In the electronic absorption and MCD spectra of the TAC and TABC species, the Q-band splits into two intense compo-

nents similarly to the 2,3-naphthalene-fused derivatives described in our preceding paper, although no significant spectral differences were observed from species to species. On the other hand, the spectra of the TAiBCs showed moderate differences depending on the structure of the isomer. The spectroscopic properties as well as the electrochemical behavior of these chlorins resemble those of the corresponding benzene-fused derivatives rather than the 2,3-naphthalene-fused derivatives. Molecular-orbital and configuration-interaction calculations within the framework of the ZINDO/S method were helpful in the discussions of the above observations.

Keywords: density functional calculations • IR spectroscopy • phthalocyanines • porphyrinoids • UV/Vis spectroscopy

Introduction

Tetraazachlorins (TACs), tetraazabacteriochlorins (TABCs), and their structural isomers, tetraazaisobacteriochlorins (TAiBCs), which have fused aromatic rings, form a new family of hydrogenated tetraazaporphyrins (TAPs) and their unique spectral properties are of interest for a wide range of applications, in a similar way to phthalocyanines (Pcs).^[1–3] Recently, we developed an approach to the synthesis of novel benzene- or 2,3-naphthalene-ring-fused TAC, TABC, and TAiBC derivatives in which mixed condensation of the corresponding precursors with different hydrogenation levels successfully yielded all of the possible derivatives; their synthesis and spectroscopic and electrochemical properties have been described in detail in our preceding paper.^[4,5] In our on-going studies, this methodology was ex-

[a] Dr. E. A. Makarova, Prof. Dr. E. A. Luk'yanets
Organic Intermediates and Dyes Institute
1/4 B. Sadovaya Str., 103787 Moscow (Russia)
Fax: (+7) 095-254-9866
E-mail: rmeluk@co.ru

[b] Dr. T. Fukuda, Prof. Dr. N. Kobayashi
Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578 (Japan)
Fax: (+81) 22-217-7719
E-mail: nagaok@mail.tains.tohoku.ac.jp

 Supporting information (experimental and calculated IR data of 1,2-NiTNTACs and 1,2-NiDNTABCs) for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

tended to the synthesis of angularly annulated 1,2-naphthalene-ring-fused TACs, TABCs, and TAiBCs, as reported in a preliminary publication.^[6] Although the angular extension of Pc skeletons was attempted as early as 1936 by Bradbrook and Linstead,^[7] the separation of mixtures of the possible structural isomers was complicated and could not be achieved. Hence, the separation and identification of the structural isomers of Pcs has been one of the most important and difficult subjects in the field of low-symmetry Pc chemistry, although recently a few studies have reported the isolation of one of the isomers of the 1,2-naphthalocyanines (1,2-Ncs). For example, Hanack et al. isolated the 1,2-FeNc(-cyclohexylisocyanide)₂ isomer with *C*_{4h} symmetry from a mixture of isomers by column chromatography.^[8] The synthetic route to the *C*_{4h} isomer of 1,2-FeNc with bulky substituents, in which steric effects suppressed the formation of the other isomers, was developed by the same group.^[9] The first successful separation of all of the possible isomers of 1,2-MgNc by chromatography has been reported recently, together with their ¹H NMR and UV/Vis spectra.^[10] Moreover, two geometrical isomers, namely, 1,2-MgNc with *C*_{4h} symmetry and 1,2-CoNc with *C*_{2v} symmetry, have also been isolated by fractional crystallization and characterized by X-ray analysis.^[11,12]

Herein we report the synthesis and separation of all the possible isomers of 1,2-naphthalene-ring-fused TACs, TABCs, and TAiBCs (**1–16**, Scheme 1), which were obtained by the mixed condensation of tetramethylsuccinonitrile (**25**) with 1,2-naphthalenedicarboxylic acid derivatives such as the anhydride, imide, and dinitrile. The isomeric structures were determined mainly on the basis of their ¹H NMR data. Spectroscopic and electrochemical methods, including UV/Vis, magnetic circular dichroism (MCD), IR, and cyclic voltammetry (CV), as well as molecular-orbital (MO) calculations, have revealed the effect of angular extension of the aromatic rings.

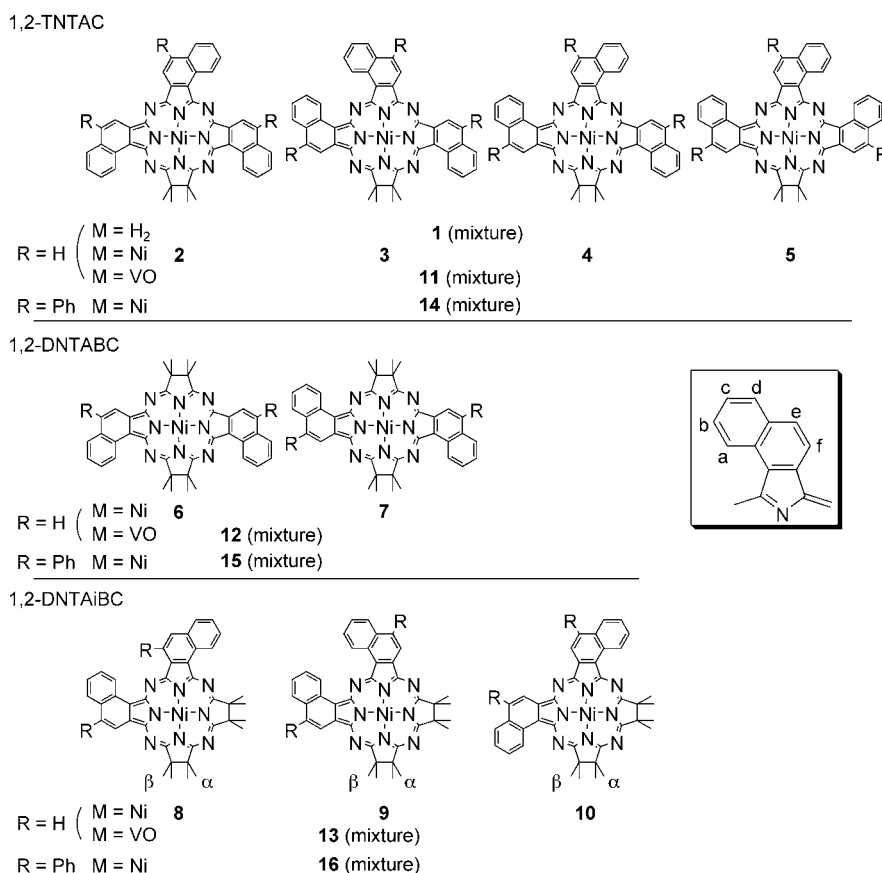
Results and Discussion

Synthesis: Derivatives of 1,2-naphthalenedicarboxylic acid, such as the anhydride, imide, and dinitrile, were used as starting compounds for the preparation of 1,2-naphthalene-fused TACs, TABCs, and TAiBCs. To synthesize 1,2-naphthalenedi-

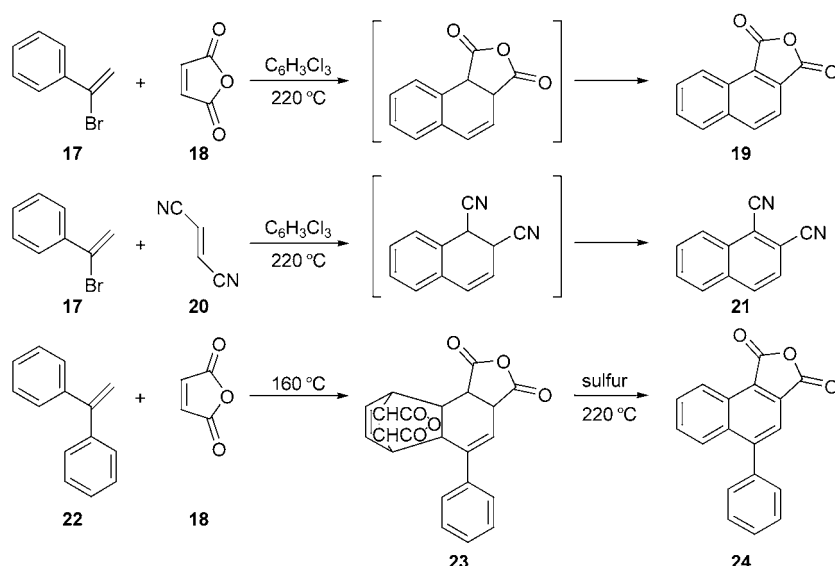
carboxylic anhydride (**19**), we reinvestigated the Diels–Alder condensation of α -bromostyrene (**17**) with maleic anhydride (**18**) in boiling toluene followed by the dehydrogenation of the resultant adduct by using sulfur.^[13] We found that the desired aromatic anhydride was formed directly in one step when the same condensation was carried out in boiling trichlorobenzene in the presence of charcoal (Scheme 2). The best yield (up to 40% after chromatography) was achieved when **17** and **18** were used in a 1:3 molar ratio. Although the yield is lower in our case, the product contains no sulfur compounds, which are frequently tedious to remove.

The condensation of the dienophile fumaronitrile (**20**) with **17** under similar reaction conditions afforded 1,2-dicyanonaphthalene (**21**) directly in 26% yield. 4-Phenyl-1,2-naphthalenedicarboxylic anhydride (**24**) was obtained according to the literature procedure^[14] by the Diels–Alder condensation of 1,1-diphenylethylene (**22**) with **18**, followed by aromatization of the thus formed bis-adduct **23** by heating with sulfur (Scheme 2).

To synthesize angularly annulated 1,2-TNTAC, 1,2-DNTABC, and 1,2-DNTAiBC, we used the strategy described in our preceding paper^[5] for the preparation of similar types of compounds with fused benzene and linearly annulated naphthalene rings, that is, by mixed condensation of precursors with different hydrogenation levels. The mixed



Scheme 1. Structures and abbreviations of the compounds in this study.



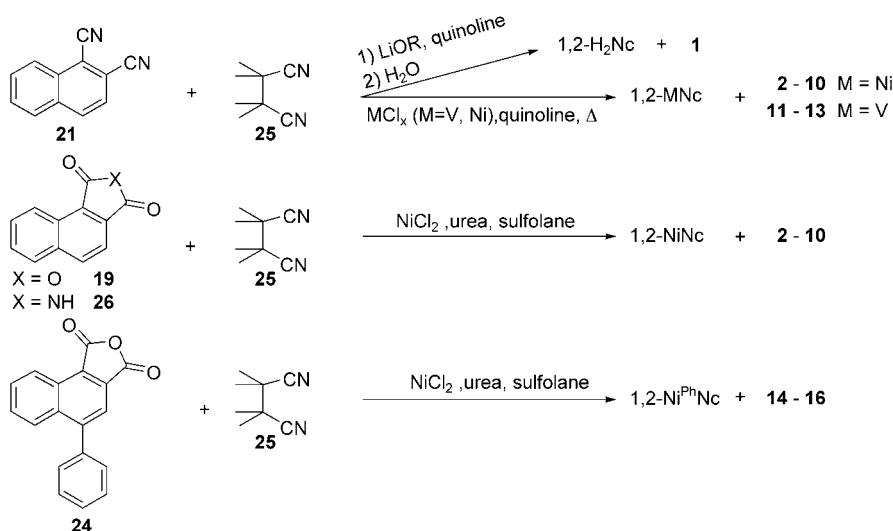
Scheme 2.

condensation of **25** with **21** was conducted in boiling quinoline in the presence of metal salts (NiCl_2 or VCl_3) or lithium 2-(dimethylamino)ethoxide (Scheme 3). The reaction of **25** and **21** in a 1:1.5 molar ratio with NiCl_2 in quinoline at 250°C for 2 h led to a mixture of 1,2-NiNc and three new compounds: 1,2-NiTNTAC (in 15% yield), 1,2-NiDNTABC (0.9%), and 1,2-NiDNTAiBC (2.0%). The condensation of these dinitriles in boiling quinoline for 6 h in the presence of lithium 2-(dimethylamino)ethoxide resulted in a mixture comprising 1,2- H_2Nc as the major product and a small amount of metal-free 1,2-TNTAC (2.1%). The desired compounds, which contain quaternary carbon atoms with methyl substituents, were easily separated from the less-soluble 1,2-Nc by extraction of the crude product mixture

with toluene and chlorobenzene, followed by further purification and separation by column chromatography on alumina.

Other derivatives of 1,2-naphthalenedicarboxylic acid, such as the anhydride or imide, can also be employed as starting materials in this reaction (Scheme 3). Their condensation with **25** was conducted in boiling sulfolane in the presence of metal salts and urea, and similarly afforded three new 1,2-naphthalene-fused compounds with similar yields to those obtained with **21**.

Since all 1,2-naphthalene-fused compounds exist as a mixture of structural isomers, unlike linearly 2,3-naphthalene-



Scheme 3.

Separation and structural characterization of the isomers: Although 1,2-NiDNTABC and 1,2-NiDNTAiBC are isomers, they can be readily characterized by analysis of their absorption spectra since their spectral band shapes are characteristic of their molecular symmetries, as described in our preceding paper.^[5] In addition, 1,2-NiDNTABC exists as a mixture of two isomers (**6** and **7**), and similarly 1,2-NiDNTAiBC and 1,2-NiTNTAC exist as three (**8**, **9**, and **10**) and four (**2**, **3**, **4**, and **5**, Scheme 1) isomers, respectively. Each isomer of 1,2-NiDNTABC and 1,2-NiDNTAiBC was completely separated by TLC and

identified by their ^1H NMR spectra. Separation of 1,2-NiTNTAC was achieved by reversed-phase HPLC. The ^1H NMR data are summarized in Table 1.

To separate the isomers of 1,2-NiDNTABC, a mixture of chloroform/hexane (1:4 v/v) was used as eluent, and each TLC sheet was developed three times. Two pink fractions with $R_f=0.21$ and 0.18 were isolated, then dissolved in chloroform, filtered and the solvent evaporated. Figure 1

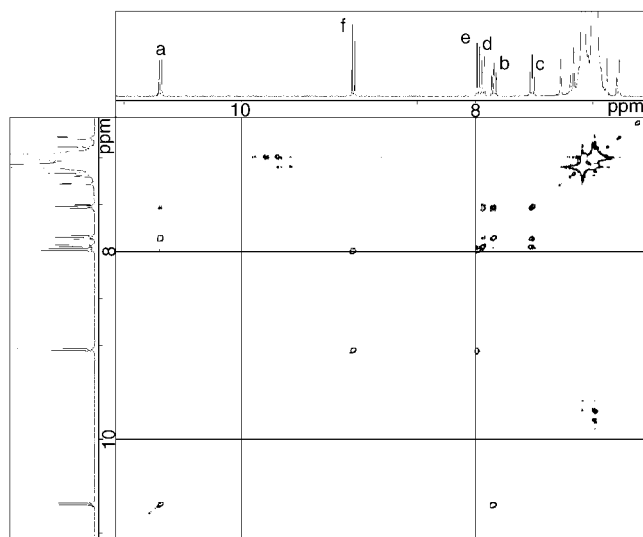


Figure 1. ^1H - ^1H COSY spectrum of **6** in $[\text{D}_8]\text{toluene}$.

shows the ^1H - ^1H COSY spectrum of **6**. The doublet signals at $\delta=10.69$ and 9.04 ppm have been reasonably assigned to protons a and f, respectively^[11] (see inset in Scheme 1). By taking through-bond interactions into consideration, the signals at $\delta=7.85$, 7.52 , 7.94 , and 7.98 ppm can be assigned to protons b, c, d, and e, respectively. Split methyl proton signals appear at $\delta=1.68$ and 1.73 ppm. The ^1H NMR spectrum of **7** is almost identical to that of **6** in the aromatic region, although the methyl protons appear at slightly differ-

ent frequencies ($\delta=1.69$ and 1.72 ppm). These two isomers were structurally assigned by performing NOE experiments on the methyl signals, that is, a through-space interaction between the two split methyl signals allowed the structures of the two isomers to be determined. As shown in Figure 2,

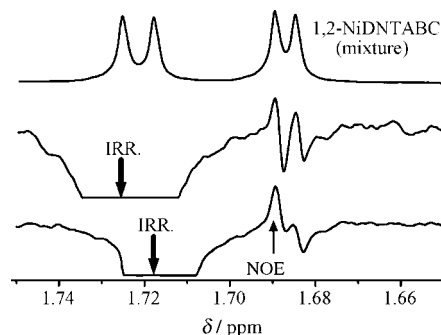


Figure 2. ^1H NMR (top) and NOE (middle and bottom) spectra of a mixture of **6** and **7**. Irradiation frequencies were set at $\delta=1.73$ and 1.72 ppm for the middle and bottom spectra, respectively.

NOE experiments were performed on a mixture of the two isomers. When the lower-field signal ($\delta=1.73$ ppm, the first fraction, **6**) was irradiated, no meaningful NOE was observed for the other signal in the region between $\delta=1.67$ – 1.70 ppm. On the other hand, irradiation of the higher-field signal ($\delta=1.72$ ppm, the second fraction, **7**) generated a detectable NOE (a positive peak at $\delta\approx 1.69$ ppm), which indicates that this signal comes from **7**. Spectral integration indicates that the mixture consists of approximately equal amounts of **6** and **7**.

The three isomers of 1,2-NiDNTAiBC ($R_f=0.31$, 0.27 , and 0.18) were similarly separated by TLC by using chloroform/hexane (2:3 v/v) as eluent. The isomer ratio was estimated to be approximately 8:1:14 for the first to third fractions, which have been attributed to **8**, **9**, and **10**, respectively, on the basis of their ^1H NMR spectra (Figure 3). The second and third fractions evidently have only one type of proton for each position on the fused-naphthalene, which in-

Table 1. ^1H NMR (400 MHz) data of the isomers of 1,2-NiTNTAC, 1,2-NiDNTABC, and 1,2-NiDNTAiBC in $[\text{D}_8]\text{toluene}$.

Compd	δ [ppm]
1,2-NiTNTAC	
2	10.99 (br, 1H), 10.73 (d, 2H), 9.25 (br, 3H), 8.12–7.81 (m, 9H), 7.57–7.53 (m, 3H), 1.83 (s, 12H)
3	11.05 (d, 2H), 10.76 (d, 1H), 9.40–9.34 (m, 2H), 9.09 (d, 1H), 8.15–7.98 (m, 9H), 7.60–7.57 (m, 3H), 1.80 (s, 6H), 1.77 (s, 6H)
4	10.90–10.87 (m, 2H), 10.68 (d, 1H), 9.13–9.07 (m, 3H), 8.07–7.84 (m, 9H), 7.62 (t, 1H), 7.53 (t, 2H), 1.82 (s, 6H), 1.79 (s, 6H)
5	10.93 (d, 3H), 9.27 (d, 1H), 9.09 (d, 1H), 9.03 (d, 1H), 8.07–7.93 (m, 9H), 7.64–7.55 (m, 3H), 1.77 (s, 12H)
1,2-NiDNTABC	
6	10.69 (d, 2H), 9.04 (d, 2H), 7.99–7.93 (m, 4H), 7.85 (t, 2H), 7.52 (t, 2H), 1.73 (s, 12H), 1.68 (s, 12H)
7	10.71 (d, 2H), 9.05 (d, 2H), 7.99–7.95 (m, 4H), 7.85 (t, 2H), 7.52 (t, 2H), 1.72 (s, 12H), 1.69 (s, 12H)
1,2-NiDNTAiBC	
8	10.84 (d, 1H), 10.49 (d, 1H), 9.14 (d, 1H), 8.85 (d, 1H), 7.99–7.80 (m, 6H), 7.55–7.48 (m, 2H), 1.55 (s, 6H), 1.50 (s, 6H), 1.40 (s, 6H), 1.39 (s, 6H)
9	10.81 (d, 2H), 8.88 (d, 2H), 7.98–7.90 (m, 6H), 7.59–7.55 (m, 2H), 1.50 (s, 12H), 1.39 (s, 12H)
10	10.48 (d, 2H), 9.10 (d, 2H), 7.98–7.93 (m, 4H), 7.81 (t, 2H), 7.50 (t, 2H), 1.55 (s, 12H), 1.40 (s, 12H)

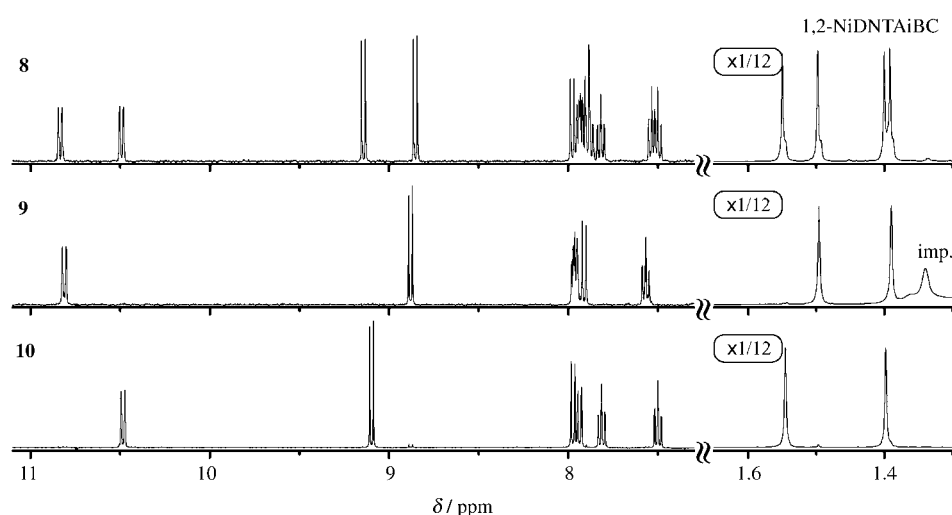


Figure 3. ^1H NMR spectra of **8** (top), **9** (middle), and **10** (bottom) in $[\text{D}_8]\text{toluene}$.

indicates the existence of a mirror plane perpendicular to the molecular plane. On the other hand, the spectral shape of the first fraction is an approximate superimposition of those of the second and third fractions. Therefore, the structure of the first fraction was unambiguously determined to be **8**. This also demonstrates that the resonance frequencies depend greatly on the local structure of the molecule. In other words, from the results of this experiment it can be claimed that the half structure divided by the plane normal to the molecular plane (i.e. the same as the mirror planes for **9** or **10**) determines the resonance frequencies, which in turn means that the aromatic protons are not affected by the other naphthalene ring, although the methyl signals are sensitive to the orientation of the fused naphthalene rings. Since the methyl resonances at approximately $\delta = 1.4$ ppm are less sensitive to the structure of the molecule than those at approximately $\delta = 1.50$ – 1.55 ppm, these resonances can be assigned to α protons (see Scheme 1). The spectrum of the second fraction shows a methyl resonance at a higher field than that of the third fraction, which indicates that a smaller loop-current effect is generated by the fused naphthalene ring. Therefore, the structure of the second fraction was assigned to **9**. In addition, it was shown that the ratio of the isomers is related to steric hindrance, and the low yield of the second fraction also implies its structure is **9** because a non-negligible steric effect must exist between the two naphthalene rings of **9** in order for skeletal deformation to occur (details of this will be discussed in the subsequent section).

Attempts were also made to separate each isomer of 1,2-NiTNTAC by using TLC, although these were unsuccessful. The complete separation of 1,2-NiTNTACs was achieved by HPLC on an octadecyl-modified silica-gel column (Shinwa Chemical Industries, Ltd.) by using chloroform/methanol (2:3 v/v) as the solvent. A flow rate of 10 mL min^{-1} gave the best separation. According to the chromatogram shown in Figure 4, the mixture consists of isomers in a ratio of

96:76:100:65 in the order of elution.^[15] Since the statistically expected yield is equivalent for all the isomers, unlike the 2,3-tetrasubstituted Pcs discussed by Hanack co-workers,^[16] the relatively low yield of the second and fourth fractions suggests that sterically hindered local structures are present, as described above for the 1,2-NiDNTAiBCs. From the ^1H NMR spectra (Figure 5) of the fractions, each isomer of 1,2-NiTNTAC can be clearly classified into two categories, that is, the first and fourth fractions and the second and third frac-

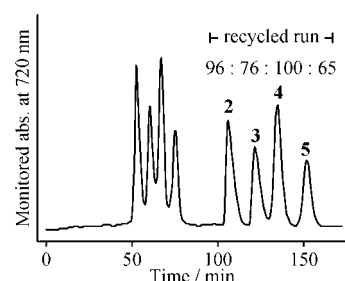


Figure 4. Chromatogram for the separation of the mixture of 1,2-NiTNTACs.

tions, depending on the methyl resonances. Since only one type of methyl proton was observed for the first and fourth fractions, their structures can be assigned to **2** or **5** (Scheme 1) because the local structure surrounding these methyl groups is symmetric. In contrast, the spectra of the second and third fractions exhibit two types of methyl group, which indicates naphthalene rings fused in different orientations. In order to distinguish the first and fourth fractions, NOE experiments were performed by irradiating the methyl resonances. As depicted in Figure 6, the first fraction shows a detectable NOE for the proton a ($\delta = 10.9$ ppm), which is not observed for the fourth fraction, which implies that the proton a of the first fraction is located closer to the methyl groups than that of the fourth fraction. On the other hand, the fourth fraction exhibits a NOE for the proton f ($\delta \approx 9.2$ ppm). These considerations, as well as the low yield of the fourth fraction, all support the conclusion that the structure of the first fraction is **2**, and therefore that of the fourth fraction is **5**. Unfortunately, the expected NOEs were not observed for the second and third fractions probably because of the very low solubility of these compounds. We concluded that the structures of the second and third fractions are **3** and **4**, respectively, on the basis of their forma-

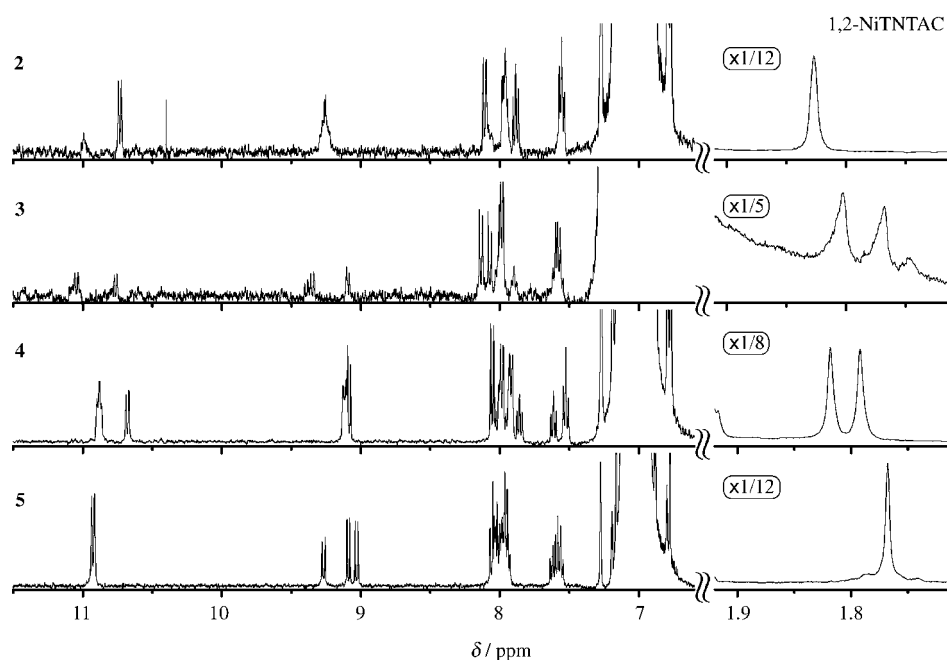


Figure 5. ^1H NMR spectra of **2**, **3**, **4**, and **5** (from top to bottom) in $[\text{D}_8]\text{toluene}$.

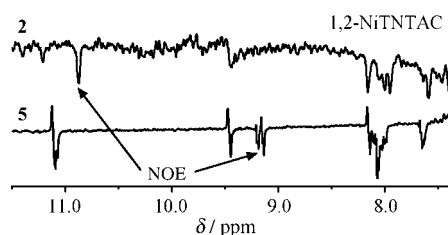


Figure 6. NOE spectra of **2** (top) and **5** (bottom) in $[\text{D}_8]\text{toluene}$. Irradiation was set at the methyl resonances.

tion ratio, although there is only circumstantial evidence for these assignments.

Molecular modeling: As briefly described in the preceding section, steric repulsion between the local structures of these molecules could possibly affect the yield of each isomer. Figure 7 depicts as examples the top and side views of the computationally optimized [DFT/6-31G(d)] structures of **9** (left) and **10** (right). The long axes of the two fused naphthalene moieties of **9** point inwards so that the two naphthalene rings may contact each other, while those of **10** point outwards. The calculations revealed that van der Waals contacts exist between the two *a* protons of **9** ($\text{H}_a\text{--H}_a$ distance, 2.07 Å). On the other hand, this type of steric repulsion was not evident in **10**, in which the $\text{H}_f\text{--H}_f$ distance was about 3.88 Å. Hence, deformation from planarity was detected for **9** as shown in the side view, although the π -conjugation plane of **10** is almost planar. Interestingly, the corresponding C_{2v} -symmetric 1,2-Nc has been reported as being practically planar, with the maximum deviation of the fused

naphthalene from the mean plane being 0.24 Å.^[12] It is conceivable that the structural perturbations at the hydrogenated sites propagate to the naphthalene-fused sites to contact two naphthalenes through the aromatic core skeleton.

IR spectroscopy: As described in our preceding paper,^[5] IR spectra reflect well the molecular structures of the tetraazachlorins and the DFT method was found to reproduce the characteristics of the spectra reasonably well. In this study, our interests focused, in particular, on whether or not each isomer can be distinguished by their IR spectra. The complexities of the IR spectra of the 1,2-naphthalene-fused derivatives

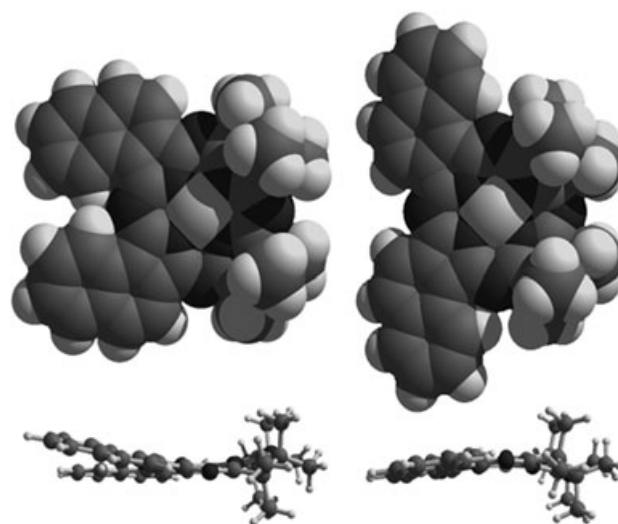


Figure 7. Optimized structures of **9** (left) and **10** (right). Top view (top) and side view (bottom) are depicted by space-filling, and ball-and-stick models, respectively.

are comparable to those of the corresponding 2,3-naphthalene-fused derivatives since both have the same number of vibrational freedoms. Both experimental and calculated results for the 1,2-NiDNTABCs (**6** and **7**) and the 1,2-NiNTACs (**2–5**) are supplied in the supporting information. Although the experimental IR spectrum of 1,2-NiNTAC was obtained for only a mixture of the four isomers owing to difficulties in preparative-scale separation, the calculations show only small differences from species to species, except for a band that appears at about 1200 cm^{-1} . Similarly, the

calculated frequencies for the different 1,2-NiDNTABCs are very similar. Nevertheless, in the latter case, there are minute differences between the calculations and the experimental spectra. For example, two frequencies were calculated at 1208 and 1196 cm^{-1} (energy difference, 14 cm^{-1}) for **6**, and the corresponding modes were estimated to be at 1203 and 1195 cm^{-1} (8 cm^{-1}) for **7**. Experimentally, these bands were detected at 1222 and 1208 cm^{-1} (14 cm^{-1}) for **6** and 1211 and 1201 cm^{-1} (10 cm^{-1}) for **7**. Similarly, the calculated frequencies at 1021 and 1015 cm^{-1} (6 cm^{-1}) for **6** shifted to 1028 and 1015 cm^{-1} (13 cm^{-1}) for **7**, reproducing the experimentally observed spectra reasonably well [1033 and 1025 cm^{-1} (8 cm^{-1}) and 1038 and 1021 cm^{-1} (17 cm^{-1}) for **6** and **7**, respectively]. Figure 8 (right) shows the calculated and experimental IR spectra of each fraction of the 1,2-NiDNTAiBCs. Unlike the other derivatives, the spectra of the different isomers are clearly distinguishable from each other. The spectra of all the isomers show a very intense band at approximately 1530 cm^{-1} , which can be ascribed to in-plane skeletal motion, including marked displacement of the *meso*-nitrogen atoms (Figure 9, bottom). Medium intensity bands observed in the spectra of **8** and **10** at about 1090 cm^{-1} appeared as a less intense band in the spectrum

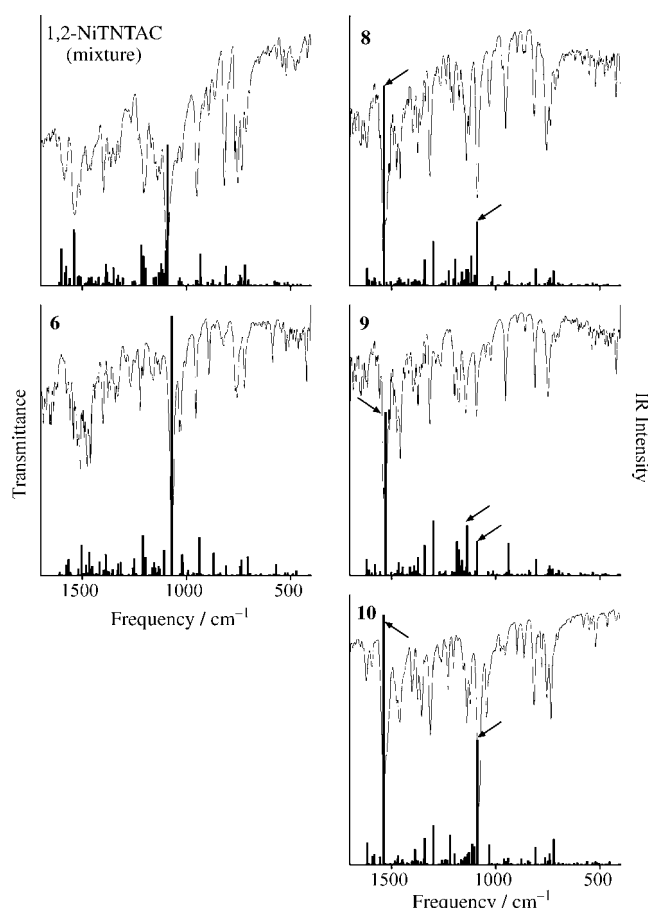


Figure 8. Experimental (solid lines) and calculated (bars) IR spectra of 1,2-NiTNTAC (left, top), **6** (left, bottom), and three isomers of 1,2-NiDNTAiBCs (**8**, **9**, and **10** from top to bottom, respectively).

of **9** at almost the same wavenumber (Figure 8, right-hand side, and Figure 9, top). Hence, the calculations closely reproduce the experimental observations, lending support to our structural assignments based on the NMR spectra. Most of the spectral features are similar to those of the corresponding benzene- or 2,3-naphthalene-fused derivatives: 1) Out-of-plane motion of the fused aromatics appear in the energy region below 1000 cm^{-1} , although their intensity is low. 2) Modes assigned to in-plane motion of the peripheral hydrogen atoms are spread over the whole spectral region. 3) The vibrational modes localized within the inner 18- π system were rarely recognized and were of low intensity.

Electronic absorption and MCD spectroscopy: Figure 10 shows the absorption and MCD spectra of all the compounds in this study. Optical data and the band-fitting parameters of the Q-bands are summarized in Table 2 and Table 3, respectively. The spectral features of these molecules resemble those of the corresponding benzene- or 2,3-naphthalene-fused derivatives.^[5] Of the split Q-band of the 1,2-NiTNTACs (left-hand side) and the 1,2-NiDNTABCs (center), the band at the longer wavelength was more intense, and the splitting energies of the bands of the 1,2-NiDNTABCs were larger. While the Q-band of the 1,2-NiDNTAiBCs (right-hand side) was sharper for the longer wavelength component, the shorter wavelength component was submerged in the adjacent vibronic and hot bands. Each isomer of the 1,2-NiTNTACs and 1,2-NiDNTABCs had an essentially identical Q-spectral envelope, but this was not the case for the 1,2-NiDNTAiBCs.

For the 1,2-NiTNTACs (**2–5**, Figure 10, left-hand side), the splitting energy of the Q-band is approximately 3240–3360 cm^{-1} , with the shorter wavelength component positioned at 596–599 nm, and the longer wavelength component at 743–745 nm. This feature resembles the corresponding benzene-fused derivative more than the isomeric 2,3-naphthalene-fused derivative. According to the Pariser–Parr–Pople (PPP) calculations reported previously, the frontier-orbital energies of 1,2-naphthalocyanines are closer to those of phthalocyanines than 2,3-naphthalocyanines,^[17] and the above observations indeed confirm that this also holds for the TACs. The intensity ratios of the absorption and MCD split Q-bands are approximately 2.6 ($=7.97/3.01$) and -0.78 ($=-5.94/7.66$), based on the D_0 and B_0 values, respectively (Table 3), which means that the longer wavelength MCD Q-band is less intense because it is energetically (and therefore magnetically) isolated from the other bands. The B_0/D_0 values also demonstrate this trend. Some slight structural dependencies are observed in the 300–500 nm region. For example, **2** has a medium intensity MCD trough at about 380 nm, which is not seen in the other spectra. These spectral characteristics are nicely predicted by the molecular-orbital calculations described in the following section.

The Q-band of the 1,2-NiDNTABCs (**6** and **7**, Figure 10, center) can be assigned by utilizing the MCD spectra. The 1,2-NiDNTABCs show large Q-band splitting energies of approximately 8120 cm^{-1} , which is much larger than those

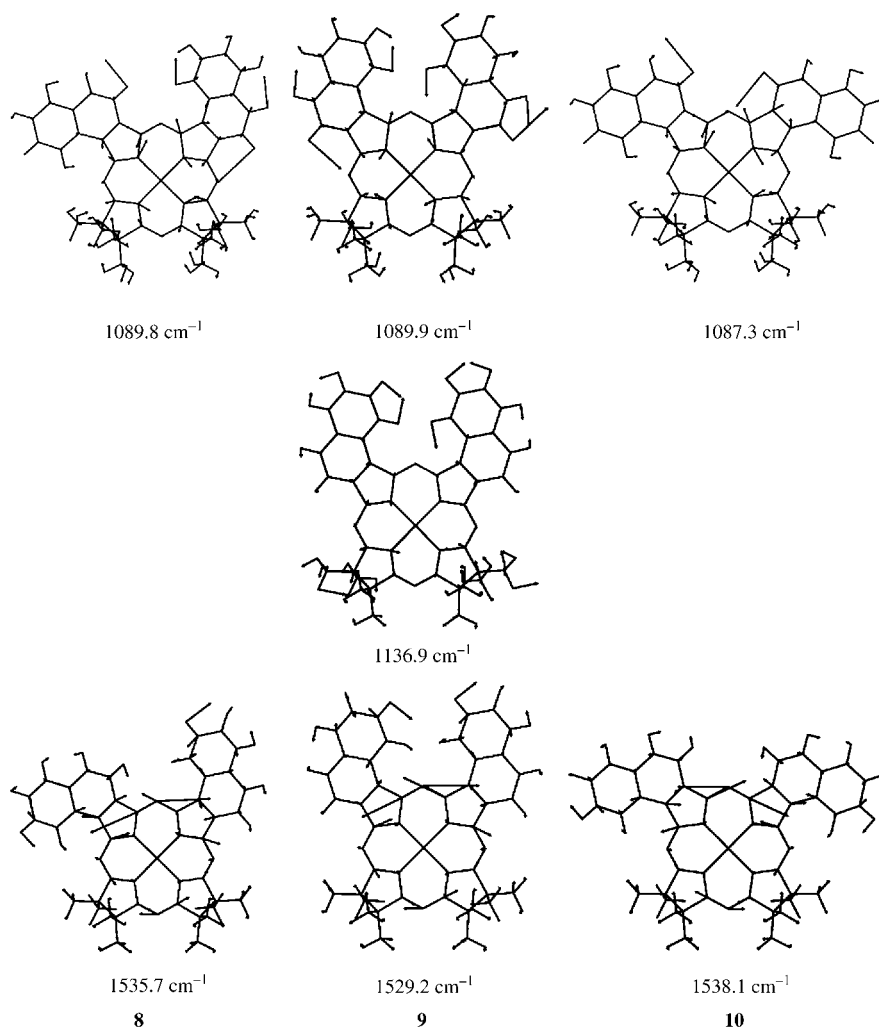


Figure 9. Atomic movements at the selected predicted frequencies.

observed for dibenzene- (ca. 6700 cm^{-1}) or 2,3-dinaphthalene-fused TABCs (ca. 4300 cm^{-1}).^[5] Hence, to the best of our knowledge, the 1,2-NiDNTABCs have the second largest Q-band splitting energy of all the Pc derivatives known to date,^[18] behind tetraazabacteriochlorin (ca. 9000 cm^{-1}).^[3a] The energy of the shorter wavelength component (513 nm) is similar to that of the benzene-fused derivative (538 nm) and the longer wavelength component (ca. 880 nm) lies between those of the benzene- (842 nm) and 2,3-naphthalene-fused derivatives (892 nm). Because of the large energy splitting of the Q-band, the MCD intensity of the longer wavelength component is very low. Band-deconvolution analysis estimated the B_0/D_0 value of the longer wavelength component to be -0.12 (Table 3), which is significantly lower than the values for the other derivatives. The spectral shapes of the two isomers are practically identical, except for slight differences in the 300–400 nm region.

Unlike the other derivatives, the 1,2-DNTAiBCs (**8–10**, Figure 10, right-hand side) show marked differences in their Q-band positions depending on the species. Since the MCD signal that corresponds to the longest Q-band is the Faraday

B term, the other coupled Q-band, which must have the opposite MCD sign,^[19,20] should appear in a higher energy region. Figure 11 shows the results of the band-deconvolution analysis of **8**. The Q_{00} -band component at the longer wavelength is readily assigned as the band at 680 nm. However, there is some ambiguity for the other coupled Q_{00} -band component at higher energy. In general, metallophthalocyanines (MPcs) show vibronic progression bands to a higher energy of the Q_{00} -band (the so-called Q_{01} -band). The energy separation between the Q_{00} - and Q_{01} -bands in normal MPcs with D_{4h} symmetry is considered to be approximately 1.1 kcm^{-1} and this also holds for MPc derivatives with other symmetries.^[21] Therefore, we assigned the band at 625 nm as the Q_{01} -band of the Q_{00} -band at 680 nm (energy separation 1.29 kcm^{-1}) and the band deconvoluted at 604 nm as the other Q_{00} -band. As described later, molecular orbital calculations, particularly the estimated energy separation of about 1970 cm^{-1} from the lower Q_{00} -band, also support this assignment (the energy separation between the Q_{00} -bands at 681 and 604 nm was determined experimentally to be ca. 1850 cm^{-1}). Although the Q-band at the longest wavelength shifts from 675 to 689 nm depending on the isomer, the spectral envelopes of isomers **8** and **9** were very similar in shape.

Electrochemistry and molecular orbital calculations:

Figure 12 displays the cyclic and differential pulse voltammograms of nickel complexes in *o*-DCB containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP); the experimental redox potentials are listed in Table 4 and Figure 13. The electrochemical data were obtained for mixtures of isomers. The second oxidation potentials were difficult to read directly from the CV curves because of the instability of the second oxidation products. Although this feature is similar to that previously reported for Nc derivatives^[18b,22–24] and 2,3-naphthalene-fused hydrogenated derivatives,^[5] this redox behavior resembles that of the benzene-fused derivatives of our preceding paper more closely.^[5] All of the couples have been assigned to ring-oxidation or ring-reduction processes. The first oxidation and reduction cou-

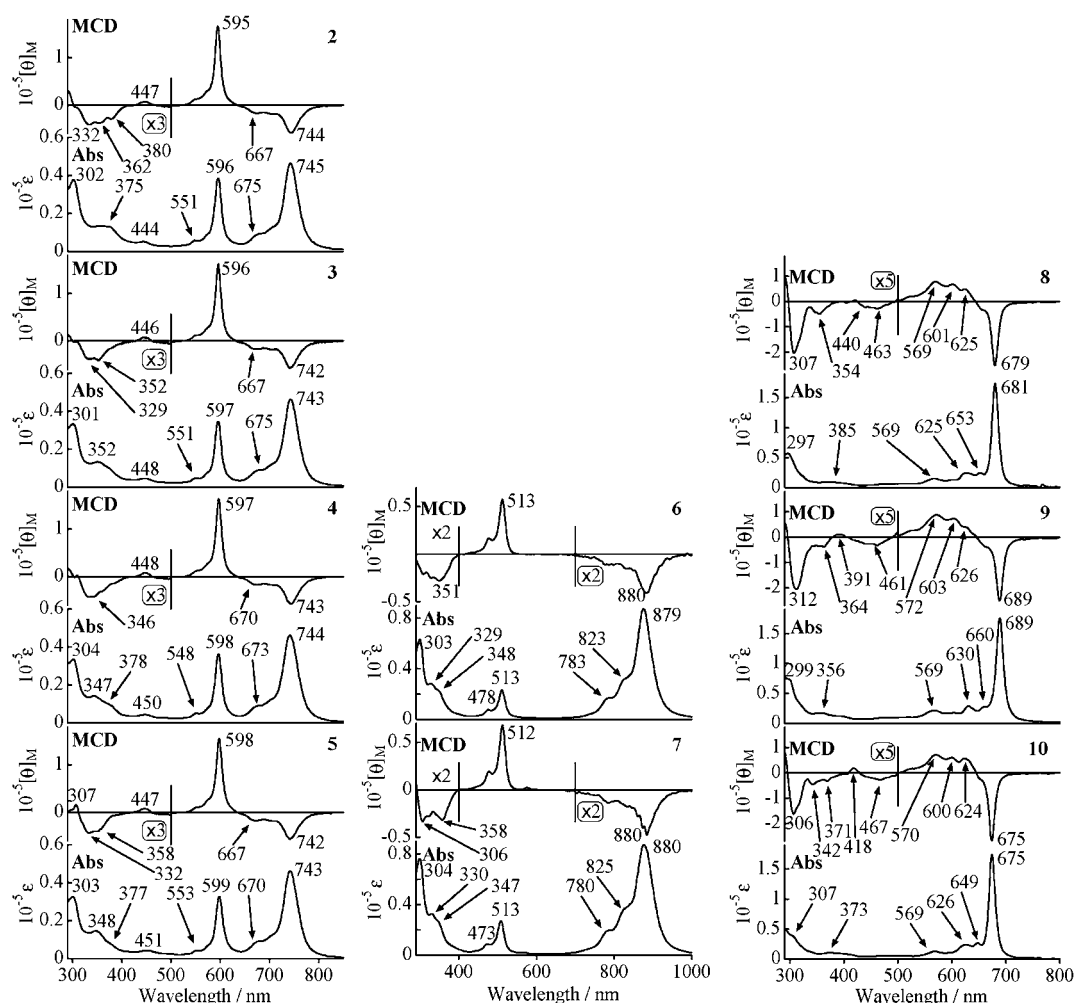


Figure 10. MCD (top) and absorption (bottom) spectra of **2–5** (left-hand side), **6** and **7** (middle), and **8–10** (right-hand side) in chlorobenzene.

ples were reversible for all the compounds. The first reduction potentials of 1,2-NiTNTAC and 1,2-NiDNTABC are similar (-1.31 ± 0.03 V), while that of 1,2-NiDNTAiBC was more negative (-1.64 V). The first oxidation potentials depend on the species; 1,2-NiDNTABC is the most prone to oxidation (-0.02 V). The potential difference, ΔE , between the first oxidation and reduction couples correlates with the HOMO–LUMO energy gaps. ΔE decreases in the order 1,2-NiDNTAiBC (1.70 V) > 1,2-NiTNTAC (1.64 V) > 1,2-NiDNTABC (1.26 V), in accordance with the order of the Q-band energies, that is, the longer wavelength Q-band shifts to the red in this order.

Molecular orbitals, transition energies, and oscillator strengths (f) were calculated by using the ZINDO/S Hamiltonian. The geometries used for the calculations were those obtained by the DFT calculations. Partial MO energy diagrams are shown in Figure 14 with calculated transition energies and oscillator strengths summarized in Figure 15 and Table 5. Similarly to the benzene- or 2,3-naphthalene-fused derivatives,^[5] the Q-bands are dominated by the HOMO $\rightarrow$ LUMO (or LUMO+1) transitions because of the large energy gaps between the HOMOs and HOMO–1s. In the

case of the TACs (i.e. **2–4**), the HOMO, LUMO, and LUMO+1 energies are very similar for the four isomers, so that the calculated Q-band energies are approximately the same. Slight differences seen in the energy region below the HOMO–2 and above the LUMO+3 give rise to the calculated spectral differences in the region around 400 nm. Comparison of the calculated results (Figure 15, left-hand side) with the experimental data (Figure 10, left-hand side) revealed that the splitting energy of the Q-band is reasonably well reproduced, although the Q-band energies are estimated to be slightly lower. No significant difference in the intensity ratio between the peaks of the split Q-bands was seen, which is also consistent with the experimental data. The two isomeric structures of the 1,2-NiDNTABCs are predicted to have identical Q-band spectra (Figure 15, middle), almost in agreement with experimental observations (Figure 10, middle). In the case of the 1,2-NiDNTAiBCs (i.e. **8–10**), the longest-wavelength Q-band appeared at different wavelengths depending on the isomers (Figure 10, right-hand side), with the trend being nicely reproduced by the molecular orbital calculations (Figure 15, right-hand side). The lower energy Q-band component shifted to

Table 2. Absorption and MCD spectral data for the 1,2-NiTNTACs, 1,2-NiDNTABCs, and 1,2-NiDNTAiBCs in chlorobenzene.

Compd	Absorption ^[a]	MCD ^[b]
1,2-NiTNTAC		
2	302(0.37), 375(0.13) 444(0.05), 551(0.06) 596(0.38), 675(0.09) 745(0.46)	332(−0.14), 362(−0.12), 380(−0.10) 447(0.02), 595(1.66), 667(−0.16) 744(−0.56)
3	301(0.33), 352(0.13) 448(0.05), 551(0.05) 597(0.34), 675(0.09) 743(0.46)	329(−0.13), 352(−0.14), 446(0.02) 596(1.62), 667(−0.17), 742(−0.57)
4	304(0.33), 347(0.14) 378(0.09), 450(0.04) 548(0.05), 598(0.36) 673(0.09), 744(0.46)	346(−0.14), 448(0.02), 597(1.63) 670(−0.17), 743(−0.58)
5	303(0.32), 348(0.15) 377(0.08), 451(0.04) 553(0.04), 599(0.33) 670(0.08), 743(0.46)	307(0.05), 332(−0.14), 358(−0.12) 447(0.03), 598(1.55), 667(−0.17) 742(−0.57)
1,2-NiDNTABC		
6	303(0.63), 329(0.28) 348(0.23), 478(0.08) 513(0.23), 783(0.17) 823(0.32), 879(0.87)	351(−0.14), 478(0.16), 513(0.58) 880(−0.20)
7	304(0.76), 330(0.33) 347(0.27), 473(0.09) 513(0.27), 780(0.19) 825(0.37), 880(0.87)	306(−0.17), 358(−0.16), 478(0.19) 512(−0.68), 785(−0.07), 880(−0.20)
1,2-NiDNTAiBC		
8	297(0.57), 385(0.10) 569(0.15), 625(0.25) 653(0.25), 681(1.74)	307(−0.41), 354(−0.10), 440(−0.05) 463(−0.06), 569(0.78), 601(0.68) 625(0.50), 679(−2.52)
9	299(0.75), 356(0.17) 569(0.22), 630(0.29) 660(0.28), 689(1.76)	312(−0.41), 364(−0.08), 391(0.02) 461(−0.07), 572(0.88), 603(0.74) 626(0.40), 689(−2.51)
10	307(0.38), 373(0.11) 569(0.13), 626(0.24) 649(0.26), 675(1.75)	306(−0.33), 342(−0.09), 371(−0.06) 418(0.04), 467(−0.06), 570(0.72) 600(0.60), 624(0.58), 675(−2.68)

[a] λ [nm] ($10^{-5}\epsilon$ [dm³ mol^{−1} cm^{−1}]). [b] λ [nm] ($10^{-5}[\theta]_M$ [deg dm³ mol^{−1} cm^{−1} T^{−1}]).

longer wavelengths in the order **10**, **8**, and **9**, while the higher-energy Q-band component showed the same trend in both experiment and calculations. As shown in Figure 14, the HOMO and LUMO+1 energy levels of the 1,2-NiDNTAiBCs are very similar (−5.495, −5.488, and −5.492 eV for

the HOMOs, and −0.987, −0.995, and −0.975 eV for the LUMO+1s of **8**, **9**, and **10**, respectively). On the other hand, the LUMO energy levels vary depending on the structure (−1.390, −1.356, and −1.422 eV, in the same order). As a result, the largest HOMO–LUMO gap is calculated for **9** (4.132 eV) and the smallest for **10** (4.070 eV). This is, however, in contrast to the calculated (and also experimentally observed) spectra, that is, the lowest- and the highest-energy Q-bands were predicted for **9** and **10**, respectively. This inconsistency can be resolved by considering the configurational interactions (CIs) between the HOMO→LUMO and HOMO−1→LUMO+1 transitions. The HOMO and LUMO+1 energies remain almost constant, while the LUMO energies change slightly depending on the structure, so that the LUMO−1~LUMO+1 energy gaps become 6.476, 6.409, and 6.519 eV for **8**, **9**, and **10**, respectively, and the energy differences between the HOMO→LUMO and HOMO−1→LUMO+1 transitions are 2.371, 2.277, and

2.499 eV for **8**, **9**, and **10**, respectively. Since larger CIs are expected for the energetically closer transitions,^[25] the largest CI of the three isomers is expected for **9**. Therefore, as a result of CIs, the lower-energy Q-band appeared at the lowest energy, even though the HOMO–LUMO gap is the

Table 3. Band-fitting parameters of the Q-bands.^[a]

Compd	ν [cm ^{−1}]	λ [nm]	$10^{-5}\epsilon_{\max}$	$\Delta\nu$ [cm ^{−1}]	$\langle\epsilon\rangle_0$	D_0	f	10^{-5}MCD int.	Band type	$\langle\epsilon_M\rangle_0$	10^3B_0	$10^3(B_0/D_0)$
2	13 406	746	0.46	710	2603	7.97	0.15	−0.53	B	−0.91	−5.94	−0.74
	16 798	595	0.37	414	983	3.01	0.07	1.49	B	1.17	7.66	2.54
6	11 288	886	0.99	657	6123	18.7	0.30	−0.19	B	−0.35	−2.29	−0.12
	19 509	513	0.22	901	1080	3.30	0.09	0.51	B	0.77	5.02	1.52
8	14 710	680	1.47	282	3003	9.19	0.19	−2.13	B	−1.32	−8.65	−0.94
	16 565	604	0.11	715	518	1.59	0.04	0.55	B	0.77	5.03	3.17
9	14 517	689	1.65	310	3748	11.5	0.24	−2.34	B	−1.61	−10.6	−0.92
	16 484	607	0.12	777	604	1.85	0.04	0.54	B	0.83	5.43	2.94
10	14 832	674	1.54	252	2795	8.56	0.18	−2.34	B	−1.28	−8.42	−0.98
	16 611	602	0.08	567	287	0.88	0.02	0.39	B	0.43	2.84	3.23

[a] ν : calculated band center energy; $\epsilon_{\max}$: extinction coefficient of the band center; $\Delta\nu$: bandwidth; $\langle\epsilon\rangle_0$: the zeroth moment of the absorption band intensity; D_0 : dipole strength in Debye units, $D_0 = \langle\epsilon\rangle_0/326.6$; f : oscillator strength; $\langle\epsilon_M\rangle_0$: zeroth moment of the B terms; B_0 : Faraday terms, $B_0 = \langle\epsilon_M\rangle_0/152.5$.

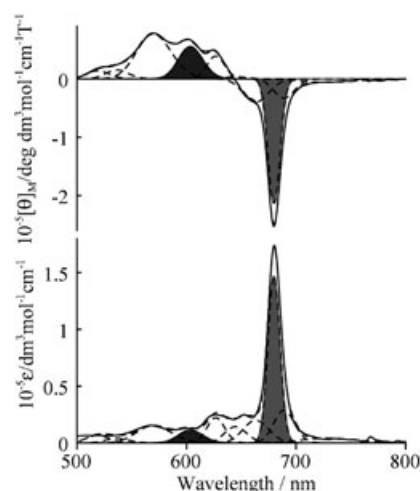


Figure 11. Simultaneous band deconvolution analysis of the absorption and MCD Q-bands of **8**. Split Q_{00} -bands are shown as shaded areas, while the experimental curves are shown as solid lines.

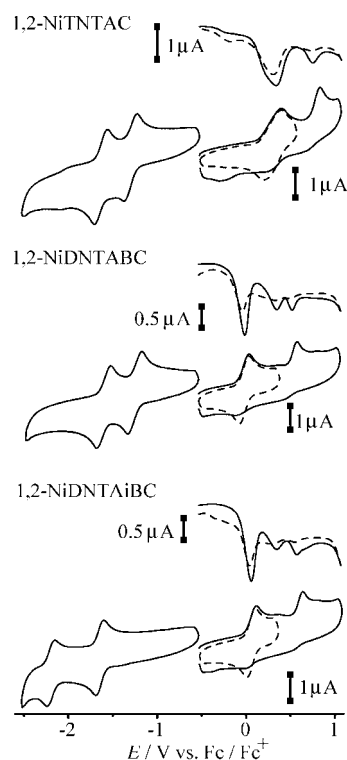


Figure 12. Cyclic voltammograms of 1,2-NiTNTAC (top), 1,2-NiDNTABC (middle), and 1,2-NiDNTAiBC (bottom) in *o*-DCB containing 0.1 mol L^{-1} TBAP. Sweep rate = 50 mV s^{-1} . All measurements were made using a mixture of isomers. Differential pulse voltammograms, in which solid lines indicate cathodic scan and dashed lines anodic scan, are also shown for the oxidation processes.

largest of the three. The coefficients of the HOMO $\rightarrow$ LUMO transitions (0.6893, 0.6889, and 0.6900, for **8**, **9**, and **10**, respectively) for the lowest-energy Q-band also support

Table 4. Redox potential data (versus Fc^+/Fc) in *o*-DCB containing 0.1 M TBAP.^[a]

Couple	$E_{1/2}$ [V]	ΔE_p [mV]
1,2-NiTNTAC		
L(0)/L(-1) ^[b]	+0.75	
L(-1)/L(-2)	+0.30	195
L(-2)/L(-3)	-1.34	80
L(-3)/L(-4)	-1.64	130
1,2-NiDNTABC		
L(0)/L(-1) ^[b]	+0.35	
L(-1)/L(-2)	-0.02	110
L(-2)/L(-3)	-1.28	110
L(-3)/L(-4)	-1.63	110
1,2-NiDNTAiBC		
L(0)/L(-1) ^[b]	+0.35	
L(-1)/L(-2)	+0.06	100
L(-2)/L(-3)	-1.64	100
L(-3)/L(-4)	-2.19	100

[a] ΔE_p represents the potential differences between the cathodic and anodic peak potentials at a sweep rate of 50 mV s^{-1} . L represents the ligand. ^[b] Data from the differential pulse voltammograms.

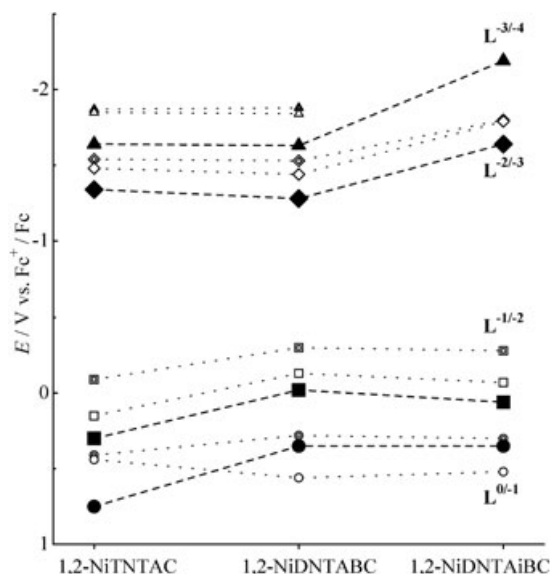


Figure 13. Electrochemically obtained redox data for 1,2-naphthalene-fused derivatives (solid marks), benzene-fused derivatives (open marks), and 2,3-naphthalene-fused derivatives (double marks).

this interpretation. That is, the smallest coefficient for **9** means that the contribution of other one-electron transitions is more significant for **9** (rather than **8** and **10**), which results in the stabilization of the lowest-energy transition state.

Conclusions

A series of 1,2-naphthalene-ring-expanded hydrogenated tetraazaporphyrin analogues, that is, 1,2-TNTACs, 1,2-DNTABCs, and 1,2-DNTAiBCs, have been synthesized. The

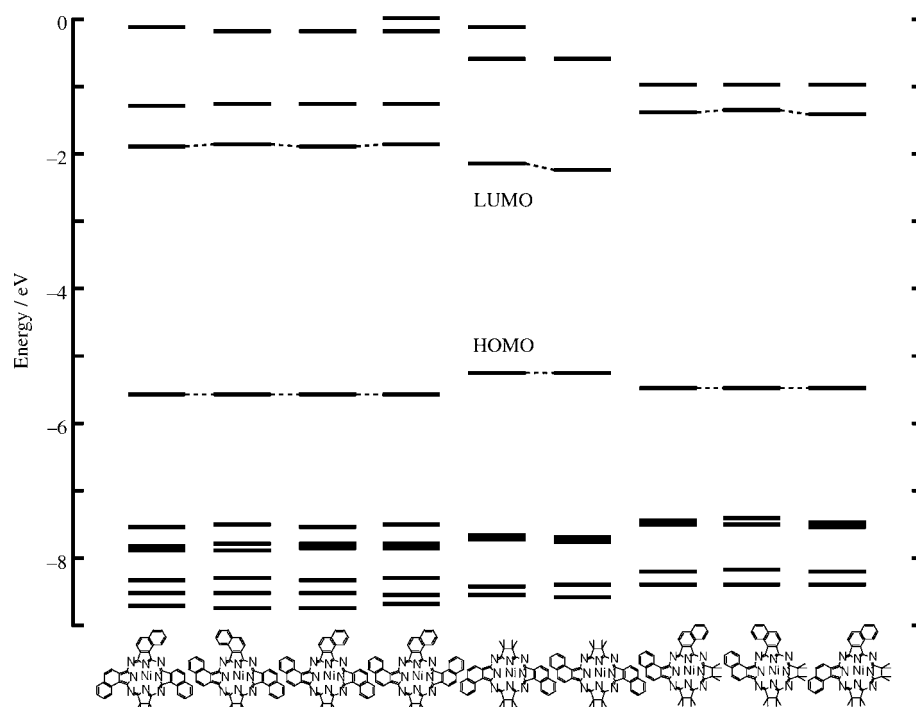


Figure 14. Partial MO energy diagrams for all the possible isomers as calculated by the ZINDO/S method.

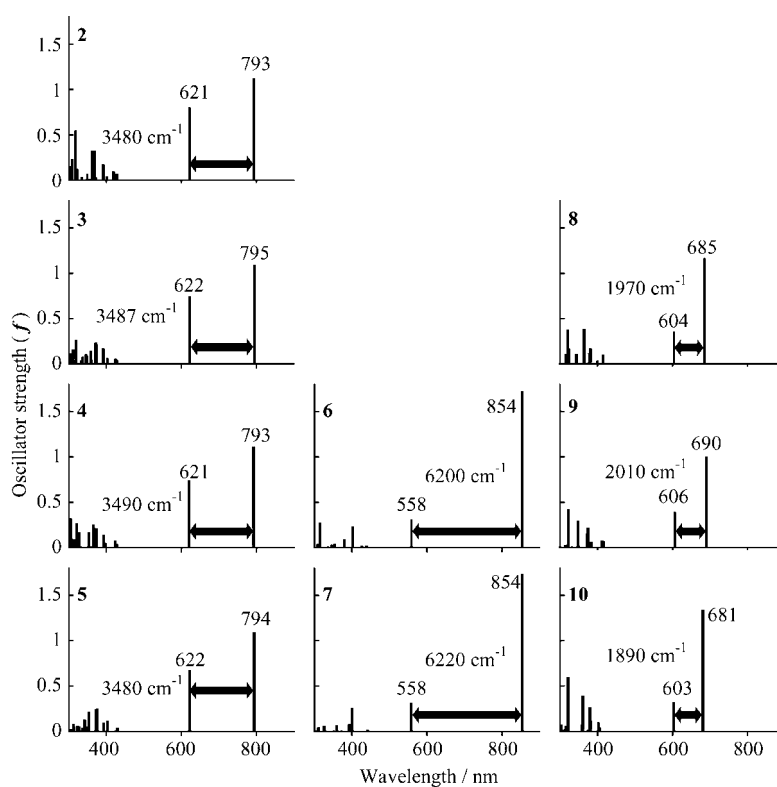


Figure 15. Calculated absorption spectra for **2–5** (left-hand side), **6** and **7** (middle), and **8–10** (right-hand side).

synthetic procedures have been carefully optimized to obtain optimal results. All of the nine possible derivatives, including four, two, and three structural isomers, of the 1,2-

NiNTACs, 1,2-NiDNTABCs, and 1,2-NiDNTAiBCs, respectively, have been successfully separated, and the structures of each isomer determined by using ¹H NMR spectro-

Table 5. Calculated transition energies and oscillator strengths(*f*).

<i>E</i> [cm ⁻¹]	<i>λ</i> [nm]	<i>f</i>	<i>E</i> [cm ⁻¹]	<i>λ</i> [nm]	<i>f</i>	<i>E</i> [cm ⁻¹]	<i>λ</i> [nm]	<i>f</i>	<i>E</i> [cm ⁻¹]	<i>λ</i> [nm]	<i>f</i>	<i>E</i> [cm ⁻¹]	<i>λ</i> [nm]	<i>f</i>
2			3			4			5			6		
12607	793	1.05	12585	795	1.09	12618	793	1.11	12602	794	1.09	11710	854	1.72
16093	621	0.79	16072	622	0.74	16112	621	0.73	16082	622	0.67	17908	558	0.30
23381	428	0.06	23343	428	0.04	23364	428	0.03	23283	430	0.03	22800	439	0.02
23866	419	0.09	23552	425	0.05	23574	424	0.07	24826	403	0.11	23441	427	0.01
24913	401	0.03	24826	403	0.06	25151	398	0.05	25439	393	0.09	24882	402	0.23
25510	392	0.16	25510	392	0.16	25452	393	0.13	26589	376	0.25	26302	380	0.08
26925	371	0.02	26788	373	0.21	26788	373	0.21	26867	372	0.24	28257	354	0.03
27093	369	0.32	26896	372	0.23	27093	369	0.18	28337	353	0.21	28910	346	0.02
27556	363	0.02	27755	360	0.04	27322	366	0.25	28620	349	0.04	31786	315	0.27
27640	362	0.31	27894	359	0.14	27716	361	0.01	29240	342	0.12	32425	308	0.03
28637	349	0.07	28620	349	0.08	28329	353	0.16	29682	337	0.03			
29824	335	0.03	28935	346	0.10	30534	328	0.16	30535	328	0.04			
30906	323	0.11	29682	337	0.07	31182	321	0.26	30950	323	0.06			
31056	322	0.12	30012	333	0.03	31766	315	0.06	31857	314	0.04			
31447	318	0.54	31338	319	0.26	32289	310	0.05	32072	312	0.07			
32383	309	0.22	31888	314	0.04	32563	307	0.09	32616	307	0.02			
32895	304	0.15	32196	311	0.15	32798	305	0.32						
			32669	306	0.11									
			33003	303	0.10									
7			8			9			10					
11708	854	1.73	14592	685	1.16	14499	690	0.99	14689	681	1.33			
17928	557	0.31	16567	604	0.35	16504	606	0.39	16576	603	0.32			
22619	442	0.01	24108	415	0.09	24033	416	0.06	24673	405	0.03			
24975	400	0.25	24988	400	0.03	24266	412	0.07	24857	402	0.09			
25471	393	0.07	26240	381	0.16	26116	383	0.06	26254	381	0.11			
27801	360	0.06	26448	378	0.11	26688	375	0.21	26530	380	0.26			
30647	326	0.06	27435	365	0.38	26838	373	0.15	26638	375	0.01			
32175	311	0.04	29104	344	0.10	28571	350	0.01	27747	360	0.39			
			30893	324	0.16	28744	348	0.29	27894	359	0.07			
			31153	321	0.37	31008	323	0.42	31114	321	0.59			
			31746	315	0.10	31319	319	0.02	31666	316	0.05			
						31878	314	0.02	32103	312	0.01			
									32992	303	0.07			

scopy and molecular models. These compounds have been characterized by various spectroscopic and electrochemical methods, including absorption, MCD, and IR spectroscopies, and cyclic voltammetry. The results of molecular-orbital calculations were used in the analysis of these physicochemical data. The main results are summarized as follows:

- 1) Synthetic procedures for the starting materials, that is, derivatives of 1,2-naphthalenedicarboxylic acid, have been reinvestigated and improved.
- 2) Metal complexes of the 1,2-TNTACs, 1,2-DNTABCs, and 1,2-DNTAiBCs have been synthesized by mixed condensation of 1,2-naphthalenedicarboxylic acid derivatives and tetramethylsuccinonitrile in quinoline in the presence of VCl₃ or NiCl₂.
- 3) TLC and HPLC techniques were successfully used to separate all of the isomers formed. ¹H NMR spectroscopy combined with the NOE method was used to characterize each isomer and, thus determine the structures of the products. The formation ratio of each isomer was rationalized in terms of the intramolecular steric repulsion effect, which is predicted by geometry optimizations at the DFT level.
- 4) DFT calculations reproduced even the observed IR spectral differences among, particularly, isobacteriochlorin structural isomers, reasonably well.
- 5) The optical and electrochemical trends resembled those of the corresponding benzene-fused derivatives rather than the 2,3-naphthalene-fused derivatives.
- 6) ZINDO/S molecular orbital and configuration-interaction calculations support the band assignments and trends in the HOMO and LUMO energies determined by the electrochemical method.
- 7) The Q-band positions of the three 1,2-NiDNTAiBC isomers are reasonably well explained by the configuration interactions between the HOMO→LUMO and HOMO-1→LUMO+1 transitions.

Experimental Section

Measurements and computational methods: Absorption, MCD, ¹H NMR (400 MHz), IR, and mass spectra, and cyclic voltammograms were obtained by following the methods described in our preceding paper.^[5] ¹H NMR (600 MHz) and NOE experiments were performed with a Bruker

AM-600 instrument using $[D_8]$ toluene as the solvent at room temperature.

Similarly, all of the computational calculations were performed in the same manner as described in the preceding paper^[5] by using the Gaussian 98 program,^[26] though in this case, an NEC TX7/AzusaA computing system operated by Tohoku University Supercomputing System Information Synergy Center was used.

Synthesis and separation: Tetramethylsuccinonitrile (**25**) was prepared according to the method described in the literature.^[27] 4-Phenyl-1,2-naphthalenedicarboxylic anhydride (**24**) was also obtained by the method described in the literature^[28] by condensation of 1,1-diphenylethylene (**22**) with maleic anhydride (**18**), followed by dehydrogenation of the resulting bis-adduct (**23**) using sulfur. 1,2-Naphthalenedicarboxylic imide (**26**) was obtained as previously described^[28] by heating 1,2-naphthalenedicarboxylic anhydride (**19**) with urea.

Thin-layer chromatography (TLC) using Merck silica gel 60 F₂₅₄ on aluminum sheets (10×10 cm) was used to separate the geometrical isomers of 1,2-NiDNTABC and 1,2-NiDNTAiBC. High-performance liquid chromatography (HPLC) was used to isolate the four geometrical isomers of 1,2-NiTNTAC by using an ULTRON VX-ODS W-type column (250×20 mm).

1,2-Naphthalenedicarboxylic anhydride (19): This compound was prepared by modification of the published method.^[13] A mixture of α -bromostyrene (**17**) (7.05 g, 0.039 mol), **18** (11.3 g, 0.115 mol), and a small amount of hydroquinone was stirred in boiling trichlorobenzene (10 mL) for 3 h (Scheme 2). HBr evolved vigorously during the reaction. Charcoal was then added and the mixture was refluxed for a further 2 h and then filtered whilst still hot. After the mixture was cooled, the trichlorobenzene filtrate was subjected to chromatography on a silica-gel column by using hexane and then hexane/chloroform (1:1 (v/v)) as eluent, and a portion with $R_f=0.25$ was collected. Recrystallization from benzene afforded the desired anhydride (2.9 g; 38%), m.p. 167°C (lit.^[13] 165–167°C).

1,2-Dicyanonaphthalene (21): The reaction was carried out according to the procedure given above for the synthesis of **19**, starting from **17** (5.9 g, 0.032 mol), fumaronitrile (**20**) (7.5 g, 0.096 mol) and a small amount of hydroquinone (Scheme 2). The trichlorobenzene filtrate was subjected to chromatography on silica gel by using hexane and then chloroform as eluent, to give the desired dinitrile (1.5 g; 26%), m.p. 190°C (from alcohol, lit.^[10] 190°C).

$\beta,\beta,\beta',\beta'$ -Tetramethyltri-1,2-naphthotetraazachlorin (1,2-H₂TNTAC, 1): A mixture of **21** (0.67 g, 3.8 mmol), **25** (0.77 g, 5.65 mmol) and lithium 2-(dimethylamino)ethoxide (0.8 g, 8.4 mmol) was stirred in quinoline (10 mL) at 250°C for 6 h (Scheme 3). After cooling to room temperature, the reaction mixture was diluted with 50% acetone (100 mL), a small amount of 5% HCl was added prior to the appearance of a precipitate, and the precipitate was filtered and washed with hot water and 50% acetone until the washings were nearly colorless. After drying, the crude residue was transferred to a Soxhlet apparatus and extracted with EtOH and then chlorobenzene. The chlorobenzene solution was concentrated to about 10 mL under reduced pressure and purified by chromatography on a silica-gel column by using chloroform as eluent. The first green fraction was collected to give, after evaporation of the solvent followed by precipitation with chloroform/ethanol of the desired compound (0.018 g, 2.1% based on 1,2-dicyanonaphthalene). MS (FAB): m/z : 673 ($[M^++1]$); elemental analysis calcd (%) for C₄₄H₃₂N₈·H₂O: C 76.50, H 4.96, N 16.22; found: C 77.02, H 5.25, N 15.30.

Nickel $\beta,\beta,\beta',\beta'$ -tetramethyltri-1,2-naphthotetraazachlorin (1,2-NiTNTAC, 2–5), nickel $\beta,\beta,\beta',\beta'$ -octamethyltri-1,2-naphthotetraazabacteriochlorin (1,2-NiDNTABC, 6 and 7), and nickel $\beta,\beta,\beta',\beta'$ -octamethyltri-1,2-naphthotetraazaisobacteriochlorin (1,2-NiDNTAiBC, 8–10). **Method a:** A mixture of **25** (0.78 g, 5.7 mmol), **21** (0.67 g, 3.8 mmol), anhydrous NiCl₂ (0.48 g, 3.8 mmol), and a catalytic amount of ammonium molybdate was stirred in quinoline (5 mL) at 250°C for 2 h (Scheme 3). After cooling to room temperature, the reaction mixture was diluted with 50% EtOH (50 mL), the formed precipitate filtered off and washed with hot water and then hot 60% EtOH until the washings were colorless. The crude residue was transferred to a Soxhlet apparatus and extracted with toluene and then with chlorobenzene. The toluene solution was evaporated to about

10 mL and purified by column chromatography on neutral alumina with toluene as eluent. Two fractions were separated and analyzed by TLC and UV/Vis spectroscopy. The first blue fraction was a mixture of 1,2-NiDNTABC and 1,2-NiDNTAiBC; the second blue-green fraction was 1,2-NiTNTAC (15 mg). Further separation of the first fraction by column chromatography on neutral alumina using toluene/hexane (1:1 v/v) as eluent gave two fractions with $R_f=0.50$ and 0.16. Chromatography of each fraction on Bio-beads S-x1 (Biorad) with chloroform as eluent afforded the desired 1,2-NiDNTABC (12 mg, 0.9%) as a pink solid and 1,2-NiDNTAiBC (25 mg, 2.0%) as a blue solid. The chlorobenzene solution was concentrated to about 10 mL and purified by column chromatography on silica gel by using chloroform/hexane (1:1 v/v) as eluent. A blue-green portion was collected, evaporated under reduced pressure, and combined with a second fraction obtained after evaporation of the toluene solution followed by precipitation by adding ethanol into a saturated CHCl₃ solution, to give the desired 1,2-NiTNTAC (140 mg, 15% based on 1,2-dicyanonaphthalene). MS (FAB): m/z : 729 ($[M^++1]$ for 1,2-NiTNTAC), 686 ($[M^+]$ for 1,2-NiDNTABC, FAB), 686 ($[M^+]$ for 1,2-NiDNTAiBC, FAB); elemental analysis calcd (%) for C₄₄H₃₀N₈Ni (1,2-NiTNTAC): C 72.45, H 4.15, N 15.36; found: C 72.64, H 4.70, N 14.64; elemental analysis calcd (%) for C₄₀H₃₆N₈Ni (1,2-NiDNTABC): C 69.89, H 5.28, N 16.30; found: C 69.88, H 5.68, N 15.43; elemental analysis calcd for C₄₀H₃₆N₈Ni (1,2-NiDNTAiBC): C 69.89, H 5.28, N 16.30; found: C 70.28, H 5.63, N 15.37.

Method b: A mixture of **25** (0.51 g, 3.7 mmol), **19** (0.5 g, 2.5 mmol), urea (0.9 g, 15 mmol), anhydrous NiCl₂ (0.48 g, 3.7 mmol), and a catalytic amount of ammonium molybdate was stirred in sulfolane (10 mL) at 250°C for 1.5 h (Scheme 3). During the reaction, a mixture of **25** (ca. 0.2 g, 1.5 mmol) and urea (ca. 0.2 g, 3.3 mmol) was added every 0.5 h. After cooling to room temperature, the reaction mixture was diluted with water, the precipitate was filtered off and washed with hot water and then hot 60% EtOH until the washings became colorless. Purification and separation of the crude residue was performed according to the procedure given above (method a), to yield 1,2-NiTNTAC (93 mg, 15%), 1,2-NiDNTABC (10 mg, 1.2%), and 1,2-NiDNTAiBC (30 mg, 3.5%). The spectral characteristics were identical to those obtained by the above method.

Method c: A mixture of **25** (0.51 g, 3.7 mmol), **26** (0.5 g, 2.5 mmol), urea (0.6 g, 10 mmol), anhydrous NiCl₂ (0.48 g, 3.7 mmol), and a catalytic amount of ammonium molybdate was stirred in sulfolane (10 mL) at 250°C for 1 h (Scheme 3). A mixture of **25** (ca. 0.2 g, 1.5 mmol) and urea (ca. 0.2 g, 3.3 mmol) was added, and the reaction continued for a further 1 h, with the temperature maintained at 250°C. After cooling to room temperature, the reaction mixture was diluted with water, the precipitate was filtered off and washed with hot water and then hot 60% EtOH until the washings became colorless. The purification and separation of the crude residue were performed according to the procedure given above (method a) to yield 1,2-NiTNTAC (88 mg, 15%), 1,2-NiDNTABC (7 mg, 0.8%), and 1,2-NiDNTAiBC (27 mg, 3.1%). The spectral characteristics were identical to those obtained by method a.

Vanadyl $\beta,\beta,\beta',\beta'$ -tetramethyltri-1,2-naphthotetraazachlorin (1,2-VOTN-TAC, 11), vanadyl $\beta,\beta,\beta',\beta'$ -octamethyltri-1,2-naphthotetraazabacteriochlorin (1,2-VODNTABC, 12), and vanadyl $\beta,\beta,\beta',\beta'$ -octamethyltri-1,2-naphthotetraazaisobacteriochlorin (1,2-VODNTAiBC, 13): The reaction was performed as described above (method a) by using **25** (0.78 g, 5.7 mmol), **21** (0.67 g, 3.8 mmol), anhydrous VCl₃ (0.65 g, 4.1 mmol), and a catalytic amount of ammonium molybdate. The reaction mixture was worked up by following method a. A toluene solution was evaporated to about 10 mL and purified by column chromatography on neutral alumina with toluene/hexane (1:2 v/v) as eluent. Two fractions were collected and after chromatography of each fraction on Bio-beads S-x1 (Biorad) with chloroform as eluent, the desired 1,2-VODNTABC (26 mg, 2.0%) and 1,2-VODNTAiBC (20 mg, 1.5%) were obtained as a lilac and blue solid, respectively. Further elution with toluene afforded a third green fraction, which was 1,2-VOTNTAC (25 mg). The chlorobenzene solution was concentrated to about 10 mL and purified by column chromatography on silica gel by using chloroform/hexane (1:1 v/v) as eluent. A major green portion was collected, evaporated under reduced pressure, combined

with the third fraction obtained after evaporation of the toluene solution, followed by precipitation with chloroform/ethanol, to give the desired 1,2-VOTNTAC (148 mg; 16% based on **21**). MS (FAB): m/z : 738 ($[M^+ + 1]$ for 1,2-VOTNTAC), 695 ($[M^+]$ for 1,2-VODNTABC, FAB), 695 ($[M^+]$ for 1,2-VODNTAiBC, FAB); elemental analysis calcd (%) for $C_{44}H_{30}N_8VO$ (1,2-VOTNTAC): C 71.64, H 4.10, N 15.19; found: C 71.56, H 4.59, N 14.55; elemental analysis calcd (%) for $C_{40}H_{36}N_8VO$ (1,2-VODNTABC): C 69.06, H 5.22, N 16.11%; found: C 68.61, H 5.46, N 15.75; elemental analysis calcd (%) for $C_{40}H_{36}N_8VO$ (1,2-VODNTAiBC): C 69.06, H 5.22, N 16.11; found: C 69.30, H 5.48, N 15.46.

Nickel $\beta\beta\beta'\beta'$ -tetramethyltri-1,2-(4-phenylnaphtho)tetraazachlorin (1,2-NiTN^{Pb}TAC, **14), nickel $\beta\beta\beta'\beta'$ -octamethyltri-1,2-(4-phenylnaphtho)tetraazabacteriochlorin (1,2-NiDN^{Pb}TABC, **15**), and nickel $\beta\beta\beta'\beta'$ -octamethyltri-1,2-(4-phenylnaphtho)tetraazaisobacteriochlorin (1,2-NiDN^{Pb}TAiBC, **16**):** The reaction was performed as described above (method *b*), starting from **25** (0.37 g, 2.7 mmol), **24** (0.50 g, 1.8 mmol) (Scheme 3), anhydrous $NiCl_2$ (0.35 g, 2.7 mmol), urea (0.66 g, 11 mmol) and a catalytic amount of ammonium molybdate (Scheme 2). After analogous work up, the crude residue was transferred to a Soxhlet apparatus and extracted with toluene. The toluene solution was evaporated to about 10 mL and purified by column chromatography on neutral alumina by using first toluene/hexane (1:1, v/v) and then by gradually increasing the content of toluene as eluent. Three fractions were collected, and each fraction was subjected to chromatography on Bio-beads S-x1 (Biorad) with chloroform as eluent. The first pink fraction afforded the desired 1,2-NiDN^{Pb}TABC (6 mg, 0.8%), the second blue fraction was 1,2-NiDN^{Pb}TAiBC (13 mg, 1.7%), and the third blue-green fraction was 1,2-NiTN^{Pb}TAC (64 mg, 11% based on 4-phenyl-1,2-naphthalenedicarboxylic anhydride). MS (FAB): m/z : 957 ($[M^+ + 1]$ for 1,2-NiTN^{Pb}TAC), 839 ($[M^+ + 1]$ for 1,2-NiDN^{Pb}TABC, FAB), 839 ($[M^+ + 1]$ for 1,2-NiDN^{Pb}TAiBC, FAB); elemental analysis calcd (%) for $C_{62}H_{42}N_8Ni$ (1,2-NiTN^{Pb}TAC): C 77.75, H 4.42, N 11.70; found: C 77.92, H 5.22, N 10.81; elemental analysis calcd (%) for $C_{52}H_{44}N_8Ni$ (1,2-NiDN^{Pb}TABC): C 74.38, H 5.28, N 13.35; found: C 74.89, H 5.21, N 13.31; elemental analysis calcd (%) for $C_{52}H_{44}N_8Ni$ (1,2-NiDN^{Pb}TAiBC): C 74.38, H 5.28, N 13.35; found: C 74.44, H 5.46, N 13.16.

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