Porphyrinoids

DOI: 10.1002/anie.200904289

Helical Bis(N-Confused Porphyrins) with Subunits Fused by Double Orthometalation with Platinum: Adaptability of an Apparently Rigid System**

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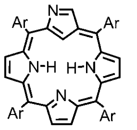
Modifications of the interior or periphery of porphyrins allow major alteration or fine tuning of the properties of the system, such as cation- or anion-binding ability, redox potential, absorption, emission, as well as many other properties. Porphyrin subunits can be also relatively easily linked into larger two- and three-dimensional arrays, thus extending the possibility of their application as biomimetic models, catalysts, and materials for the transport of charge, molecules, and ions. Among the covalently[1] and coordinately[2] linked oligomers, the most attractive class is constituted by the systems in which the subunits are directly linked.[3] The interaction between delocalized π-bond systems appears to be strongest when the β-pyrrole carbon atoms of the porphyrins are linked. An important feature of β–β-linked bis(porphyrins) is their intrinsic axial chirality. However, the stability of the configuration requires restriction of the rotation around the β–β-bond. This restriction can be provided by the appropriate choice of metal ion that coordinates within both macrocyclic cores.[4] The external nitrogen atom of the confused pyrrole in N-confused porphyrin (NCP) **1**[5] and some of its derivatives[6] and complexes[7] can act as a donor site.[8] In the readily obtainable bis(N-confused porphyrin) **2**,[9] a *cis*-oriented system of two external nitrogen atoms can potentially serve as a chelating ligand, and coordination of an inert metal ion in this site may prevent rotation and preserve configuration of the molecule. Platinum(II) is thus a metal ion of choice because of its tendency to form inert *cis* complexes that consist of a five-membered chelate ring.



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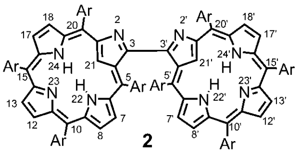

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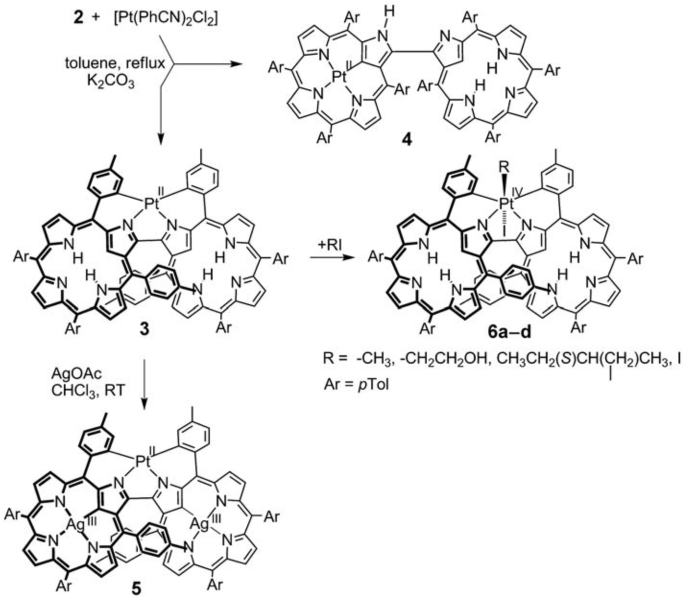
Reaction of bis(NCP) **2** with [Pt(PhCN)Cl$_2$] yields two isomeric platinum-containing complexes with different coordination modes (Scheme 1). Heating **2** at reflux with an equimolar amount of [Pt(PhCN)$_2$Cl$_2$] in the presence of potassium carbonate in toluene for two days resulted in formation of **3** as the main product (about 50 %), as well as the monoplatinated insertion product **4** (10 %). In both cases, the composition of the complex was established by ESI MS (*m*/*z* 1532), which indicates the presence of one platinum ion and one bis(NCP) unit. Compound **3** constitutes the first example of a bis(porphyrinoid) complex that consists of a metal ion coordinated by double orthometalation.[10] The twofold symmetry of the ^{1}H NMR spectrum of **3** (CDCl$_3$, 213 K) reveals the same coordination mode for both subunits. The higher-field signals of protons bound to the internal carbon atom C21 at $\delta = -3.41$ ppm and those attached to the internal nitrogen atoms N22 and N24 ($\delta = 1.19$ and $\delta = -0.05$ ppm, respectively) indicate that the porphyrin cores are not occupied by metal ions. A doublet signal at $\delta = 8.10$ ppm with $^4J = 1.8$ Hz is attributed to the *meta* proton in the vicinity of the deprotonated coordinating carbon atom of the *para*-tolyl substituents on C20 of both subunits. This



Scheme 1. External and internal metalation of bis(NCP) **2** with platinum(II), insertion of silver(III) into the externally platinated bis(NCP) **3**, and oxidative addition of iodine or iodoalkyls to **3**.

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[**] This work was supported by the Ministry of Science and Higher Education under Grants PBZ-KBN-118/T09/2004 and N N204 029035.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200904289.

observation is consistent with orthometalation of the tolyl rings,[10b] while the upfield shift of the 5-tolyl *ortho*, *meta*, and methyl proton signals ($\delta = 6.59$, 5.28, and 0.64 ppm, respectively) indicate that orientation of the subunits is similar to that observed in the free ligand **2**.[4c,9]

The ^{1}H NMR spectrum of **4** ($CDCl_3$, 213 K) indicates an asymmetric structure of the system. The spectrum consists of features typical of a free-base NCP (internal CH and NH signals at $\delta = -4.91$, -2.47, and -2.07 ppm) and those of its complexes with divalent Group 10 metals (signal for 2-NH at $\delta = 10.46$ ppm).[5a,8a,10b] The geometry of the molecular skeleton of **4** is not drastically altered with respect to that of **2** or **3**, as can be inferred from the upfield shifts of some of the protons caused by the aromatic ring current of the neighboring subunits.[9,11]

Reaction of **3** with silver(I) acetate under very mild conditions yields an insertion product **5**, which consists of macrocyclic subunits that are both metalated with silver(III) (Scheme 1). A peak at *m*/*z* 1743.36 in the MALDI spectrum of **5** is consistent with its composition, while NMR spectra reveal persistence of the twofold symmetry. The lack of the "internal" protons and spin–spin coupling of β-pyrrole protons with ^{107,109}Ag indicate coordination of diamagnetic d^8 silver(III) ions within the porphyrin cores.[7b,11,12]

An oxidative addition[13] of methyl iodide to **3** provided the iodomethylated complex **6a** quantitatively within one hour at room temperature, although for 2-iodoethanol, two days were required under the same conditions to obtain **6b** and, for the reaction with 1-iodo-2-(*S*)-methylbutane, heating of a toluene solution at 90 °C for about 20 hours was necessary to obtain **6c** in good yield (Scheme 1). The original twofold symmetry of **3** is lost in the iodoalkylated complexes because of the non-equivalency of the faces of the compounds, and is reflected by the ^{1}H NMR spectra of **6a–c**, as each spectrum consists of two sets of NCP signals (Figure 1). The unique resonance of an apical methyl group at $\delta = 1.71$ ppm in the spectrum of **6a** is accompanied by two broader platinum satellites spaced by $^2J_{\mathrm{HPt}} = 70$ Hz. Also, signals for the two meta protons of the orthometalated aryl groups indicate ^{1}H–^{195}Pt coupling ($^3J_{\mathrm{HPt}} = 31$ and 36 Hz). A ^{13}C–^{195}Pt coupling ($^1J_{\mathrm{CPt}} = 638$ Hz) can be observed for the methyl carbon atom in the ^{1}H–^{13}C HSQC spectrum. Similar features are also present in the spectra of **6b** and **6c** (Figure 1). Oxidative addition of iodine to **3** proceeded immediately after mixing the starting materials. The high-resolution ESI mass spectrum of the product **6d** (*m*/*z* 1786.3645) reveals the presence of two iodide ligands per molecule. The ^{1}H NMR spectrum of **6d** resembles the spectra of the iodoalkylated species, except for the obvious lack of the alkyl signals and appearance of only one set of the ligand resonances, owing to the twofold symmetry of the bis(iodide) complex.

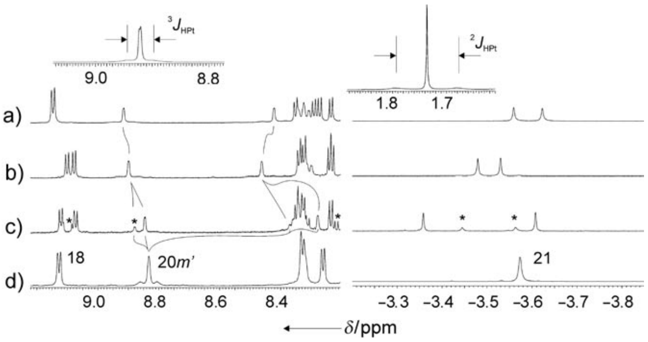

Figure 1. Low- and high-field regions of the ^{1}H NMR spectra (600 MHz, $CDCl_3$, 300 K) of platinum(IV) complexes **6a** (a), **6b** (b), **6c**, (c), and **6d** (d). Positions of the *meta*-proton resonances of the orthometalated *para*-tolyl groups (20*m*′) are joined by the curved lines. The insets in spectrum (a) (**6a**) show expansions of the signals of 20*m*′ and the apical methyl protons with platinum satellites. The asterisks above spectrum (c) indicate positions of some of the resonances of the minor diastereomer of **6c**.

The single-crystal X-ray diffraction analysis[14] of **6a** reveals the coordination of both methyl and iodide groups, as well as two external nitrogen and two *ortho* carbon atoms, to the metal center (Figure 2). The equatorial environment of the platinum ion is essentially planar, with donor atoms lying alternately over and under the mean plane defined by the N_2C_2Pt atom system, with displacements of less than ± 0.1 Å. The whole system is helical and the unit cell contains a symmetry-dependent pair of enantiomers. Similar structural features are observed for the bis(iodo) complex **6d** (see the Supporting Information).[14] The molecule's skeleton adopts a stretched Z shape, in which the porphyrin subunits are almost parallel to each other with a dihedral angle between the mean planes of only 1.91(7)° in **6a** and 5.1(1)° in **6d**, and a dihedral angle of about 55° between these planes and the N_2C_2Pt plane in both complexes.

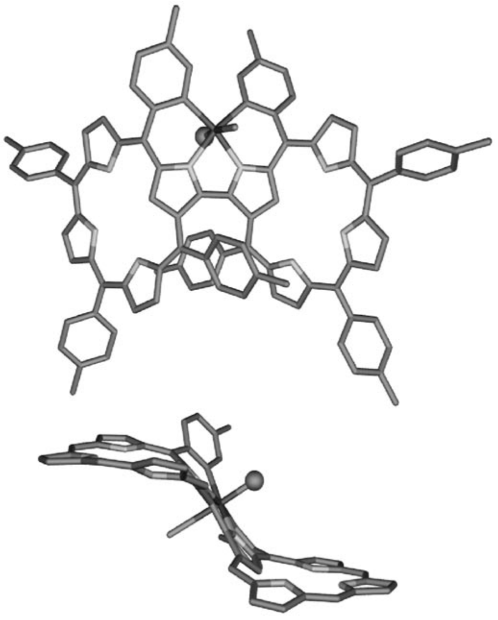

Figure 2. Stick representations of the molecular structure of **6a**. The position of the methyl ligand is marked with a sphere. All hydrogen atoms are omitted. The lower view shows the stretched Z shape of the molecule; all aryl groups are omitted except for the orthometalated groups.

The optical spectra of the macrocycles are strongly affected by the external coordination of the platinum ion (see Figure S51 in the Supporting Information). The broad band centered at 982 nm observed for **3** is absent in the spectrum of isomeric **4** or the ligand **2**. Also, the spectra of the platinum(IV) complexes **6a–e** exhibit relatively strong bands between 800 and 1000 nm. These features, together with the considerable splitting of the Soret-type band in the spectra of **3**, **5**, and **6** suggest the presence of more effective interactions between the π-electron systems of aromatic subunits in these complexes than in the nonfused **2** or **4**.

Systems **2–6** are intrinsically chiral because of their helical structures. The configuration stability is provided by fusion of the subunits with coordinated platinum ions in **3**, **5**, and **6**. We succeeded in enantiomer separation for the systems **3** and **5** by means of enantiomer-resolving HPLC, and obtained about 96% *ee* for each fraction. The nonracemic **6a** or **6d** could be obtained by addition of MeI or iodine, respectively to the separated enantiomers of **3**. Metalation of the enantiomers of **3** with silver(III) leads to the respective stereoisomers of **5**. The sign of the Cotton effect in the CD spectra of each enantiomer of **3** is preserved in those of derivatives **6a** and **6d** (Figure 3), thus indicating helicity retention upon oxidative addition.[15] A very slow racemization at room temperature could be observed for a solution of a pure enantiomer of **3** in chloroform, and results in the appearance of about 15% of the other stereoisomer after 50 days, as established on the basis of the HPLC analysis. The racemization process accelerates in a benzene solution heated to 80°C to yield a racemic mixture after 24 h. Apparently, the isomerization takes place even though the rotation of the subunits is disabled by double chelation of the platinum ion. Molecular modeling studies and DFT calculations were used to create a structural model, which has an energy 23 kcal mol^{-1} above the optimized Z-shaped arrangement of **3** and adopts a U shape that allows the subunits to exchange their positions, and may result in racemization (see the Supporting Information for details). Racemization upon crystal growth at room temperature from the solution of enantiopure **6a** prevents assignment of the absolute configuration of the complex by X-ray crystallography, but indicates the flexibility of systems that contain platinum(IV) complexes.

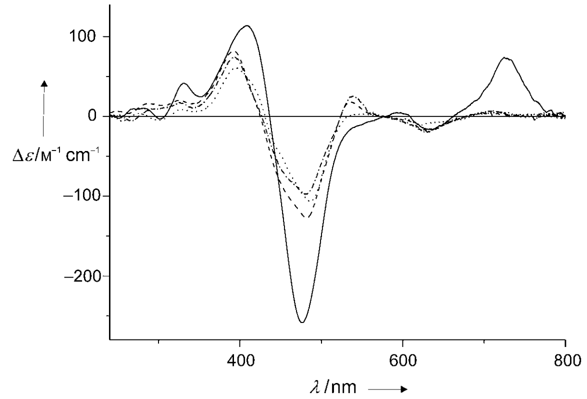

Figure 3. CD spectra (CH_2Cl_2, RT) of the slower migrating enantiomers of **3** (——), the product of the reaction of **3** with MeI **6a** (-----) and with I_2 **6d** (•••••), and **6c**, that is, the product of the reaction of racemic **3** with 1-iodo-2-(*S*)-methylbutane (–•–•). The CD spectra for the pairs of enantiomers of the complexes **3**, **5**, **6a**, and **6d** are given in the Supporting Information (Figure S52–S55).

The unexpected flexibility of the platinum-fused bis(NCP) is reflected by its accommodation of a chiral carboanion to form **6c**. The reaction of a racemic solution of **3** with enantiopure 1-iodo-2-(*S*)-methyl-butane was monitored by ^{1}H NMR spectroscopy and proceeded slowly at room temperature to give initially an equimolar mixture of diastereomers of **6c** (about 5% of conversion after 5 h) but, during a 10 day period, the ratio of diastereomers altered from 1:1 to 1:0.6 and the overall substrate conversion rose to 50%. When the reaction was carried out in toluene at 90°C, a full conversion of **3** with about a threefold molar excess of one of the diastereomers was obtained after 18 h of heating.[16] Further enhancement of the diastereomeric excess (up to 0.8 molar ratio of the major component) could be achieved by heating a solution of **6c** without the chiral alkyl iodide in chloroform at 40°C for two days. The CD spectrum of **6c** closely resembles that of one of the enantiomers of **6a** or **6d** (Figure 3). Evidently, the chiral alkyl ligand induces unidirectional alteration of the helicity of the bis(porphyrin) system after coordination to the platinum(IV) ion.

In conclusion, we have shown the formation of a helical bis(NCP) system in which the subunits are fused by peripheral coordination and double orthometalation of platinum(II), which stabilizes the configuration of the system and facilitates separation of the enantiomers. The subunits retain their ability to coordinate trivalent metal ions within the macrocyclic interior. An efficient oxidative addition to form hexacoordinated platinum(IV) complexes allows further modification of the system. The system can undergo chiral induction owing to the adaptive properties of the platinum-fused bis(porphyrin). The potential of the system in the synthesis of new chiral catalysts by insertion of redox-active metal ions into the porphyrin cores is currently under investigation.

Received: August 1, 2009

Keywords: helical structures · orthometalation · oxidative addition · platinum · porphyrinoids

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[10] In the dimeric platinum(II) complexes reported previously for NCP or its alkylated nickel(II) complexes, one of the subunits coordinates through the external nitrogen atom of the confused pyrrole and through an *ortho*-carbon of the adjacent aryl ring, while the other subunit coordinates solely through the external nitrogen atom. Consequently, the overall symmetry of the system is C_1; see: a) H. Furuta, K. Youfu, H. Maeda, A. Osuka, *Angew. Chem.* **2003**, *115*, 2236–2238; *Angew. Chem. Int. Ed.* **2003**, *42*, 2186; b) P. J. Chmielewski, I. Schmidt, *Inorg. Chem.* **2004**, *43*, 1885. In the case of **2**, analysis of the reaction intermediates by mass spectrometry and ^{1}H NMR spectroscopy reveals formation of two isomeric unsymmetrical platinum complexes of **2**. The ESI mass spectra of the reaction mixture taken after 20 h of the reaction show the presence of "tetrameric" species, that is, complexes that consist of two bis(NCP)s, two platinum ions, and two chloride ions. When the reaction is carried out without any proton scavenger, tetramers that are difficult to separate from each other are formed. However, the mixture can be easily converted into **3** by heating a solution of the tetramers in toluene to reflux in the presence of K_2CO_3 without an additional platinum source.

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[14] Crystal data for **6a**: $C_{97}H_{75}IN_8Pt\cdot 0.792(C_6H_{14})\cdot 3.264(CHCl_3)$, $M_r = 2132.35$, $T = 100$ K, MoK_α radiation, triclinic, space group $P\bar{1}$, $a = 15.798(5)$, $b = 17.063(7)$, $c = 19.413(8)$ Å, $\alpha = 70.56(3)$, $\beta = 88.54(3)$, $\gamma = 88.51(3)$, $V = 4932(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.436$ Mg m^{-3}, $\lambda = 0.71073$ Å, $\mu = 2.05$ mm^{-1}, $F(000) = 2146$, KUMA KM4 CCDK-geometry Diffractometer with Sapphire CCD detector, $3.0 \leq \theta \leq 36.8°$, 58578 collected reflections, 30072 independent reflections, 1193 parameters, $R1(F) = 0.063$, $wR2(F^2) = 0.164$, $S = 1.03$, largest difference peak and hole 2.08 and −1.98 e Å^{-3}. Crystal data for **6d**: $C_{96}H_{72}I_2N_8Pt\cdot 1.5(C_6H_{14})\cdot 2(CHCl_3)$ $M_r = 2154.50$, $T = 100$ K, Mo$_{K\alpha}$ radiation, triclinic, space group $P\bar{1}$, $a = 15.718(8)$, $b = 17.188(9)$, $c = 18.920(9)$ Å, $\alpha = 71.72(5)$, $\beta = 86.01(5)$, $\gamma = 88.19(5)$, $V = 4841(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.478$ Mg m^{-3}, $\lambda = 0.71073$ Å, $\mu = 2.30$ mm^{-1}, $F(000) = 2158$, diffractometer Oxford Diffraction Xcalibur PX with Onyx CCD detector, $4.1 \leq \theta \leq 38.5°$, 51664 collected reflections, 22166 independent reflections, 1132 parameters, $R1(F) = 0.078$, $wR2(F^2) = 0.190$, $S = 1.01$, largest difference peak and hole 3.50 and −1.70 e Å^{-3}. CCDC 742635 (**6a**) and 742636 (**6d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] This result contrasts with other helical bis(porphyrin)systems coordinated platinum ions, where the change of oxidation state and coordination number is combined with helicity inversion, see: S. Yamaguchi, T. Katoh, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 14440.

[16] Formation of a small fraction (10–15%) of the bis(iodide)complex **6d** can be observed upon reaction of **3** with 1-iodo-2-(S)-methyl-butane carried out at elevated temperatures. Compound **6d** can be easily separated from **6c** by column chromatography. Interestingly, **6d** formed under such conditions displays optical activity expressed as molar CD amplitude, which is about 20% of that recorded for **6d** obtained from nonracemic **3**.