

# Skeletal modification of a non-planar phthalocyanine analogue under very mild conditions†

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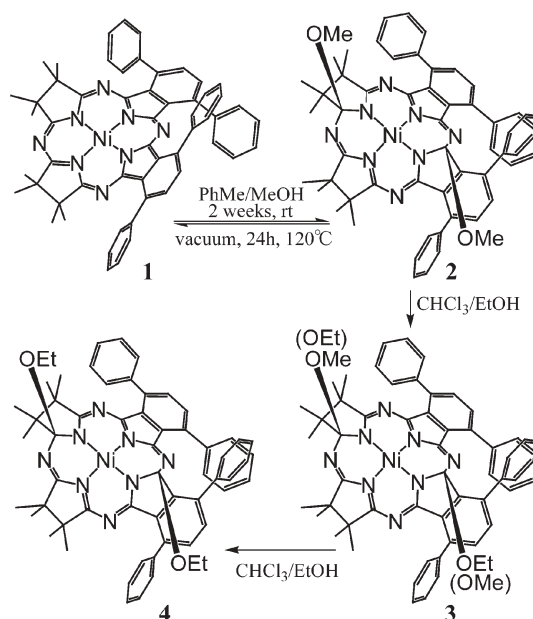
A sterically congested tetraphenyl-substituted dibenzo-tetraaza-isobacteriochlorinato nickel derivative unexpectedly reacts with methanol at room temperature to release internal molecular strains, leading to the formation of a ligand having a skeleton bearing two *cis*-methoxy substituents.

Phthalocyanines (Pcs) have an  $18\pi$  electron aromatic system with flat molecular structures. Since their accidental discovery in the early 20th century,<sup>1</sup> Pcs have contributed significantly to the dye and pigment industries due to their prominent applicability. The versatile spectroscopic and electrochemical properties of Pcs have also attracted the interest of researchers in many other areas, such as optical devices, catalysts, electrical conductors, photodynamic cancer therapy, and chemical sensors.<sup>2</sup> It is well known that the chemical and physical stabilities of typical Pcs are excellent. For example, commercially available CuPc is soluble in conc.  $\text{H}_2\text{SO}_4$  without decomposition, and sublimes with increasing temperature under vacuum. This robustness, however, restricts the chemical modification of Pcs under mild conditions, so that Pc core modifications have rarely been reported. Recently, McGaff and coworkers have reported that solventothermal reactions of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  with 1,2-dicyanobenzene in alcohol yielded 14,28-di-alkoxy-substituted Pc derivatives.<sup>3,4</sup> They concluded, however, that the formation of the alkoxy-substituted derivatives occurs during the Pc synthesis as intermediates. Hence, the modification of the Pc cores in this case occurs as they form, rather than following the formation of unsubstituted Pcs. 1,2-dicyanobenzene reacts with indium metal to give the 14,28-bicycloPc derivative,<sup>5,6</sup> although transformation of Pc into the bicycloPc has not been achieved. As another example, the reaction of  $\text{TiPcCl}_2$  (or  $\text{NbPcCl}_2$ ) and  $\text{Na}_2\text{Pc}$  at 190 (220) °C in chloronaphthalene gives 'stapled'  $\text{TiPc}_2$  ( $\text{NbPc}_2$ ).<sup>7</sup> These results imply that the 14 and 28 positions are relatively reactive compared to the other segments of the Pcs during synthesis, but that once the Pcs are formed, these positions are no longer active.

Tetraazaisobacteriochlorin (TAiBC) is a Pc analogue, in which two adjacent pyrrole  $\beta$ -carbons are chemically dehydrogenated. Recently, dibenzo-fused stable TAiBC has been isolated by employing tetramethylsuccinonitrile as one of the starting materials.<sup>8</sup> The X-ray analysis revealed that the geometry of the dehydrogenated pyrrole sites deviates slightly from planarity due

to the presence of tetrahedral  $\text{sp}^3$ -hybridized carbons. In addition, we have clarified that the introduction of phenyl groups in the, so-called, adjacent  $\alpha$ -positions produces highly deformed non-planar Pcs.<sup>9</sup> Both of these two types of Pc analogue have, in common, structural deformations in the aromatic core. These deformations increase the intramolecular stresses, and reduce the resonance energy relative to the corresponding planar analogues. In this study, we have observed that the combination of dehydrogenation and phenyl-substitution imparts unusual chemical properties to Pcs, such that tetraphenyl-substituted di-benzo TAiBC (**1**) shows interesting chemical reactivities to methanol under very mild conditions (Scheme 1).

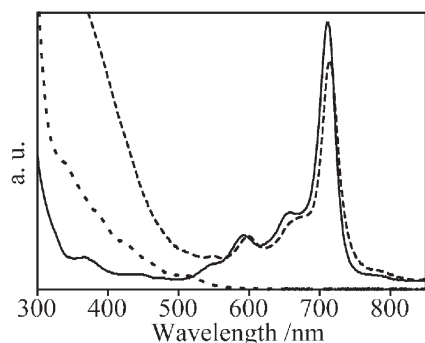
Mixed condensation of 3,6-diphenylphthalonitrile<sup>10</sup> and tetramethylsuccinonitrile<sup>11</sup> in the presence of  $\text{NiCl}_2$  yielded three possible macrocycles, *i.e.* tetraazachlorin (TAC), tetraazabacteriochlorin (TABC), and TAiBC, **1**.<sup>12</sup> Nickel was chosen for synthetic reasons.<sup>8</sup> The mixture was first purified by column chromatography in order to remove unassignable by-products, and TAC and TABC were then removed by stepwise extraction using hexane and methanol, respectively. Compound **1** is moderately soluble in both hexane and methanol, while TAC and TABC are very sparingly soluble in hexane or methanol, respectively. Fig. 1 (solid line) shows the absorption spectrum of **1** in toluene. The Q band appears at 711 nm, red-shifted by *ca.* 40 nm from the



Scheme 1 Chemical reactivities of **1** and **2**.

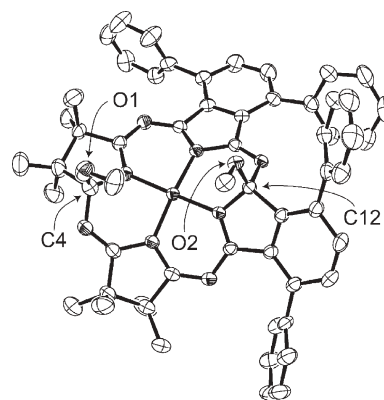
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**Fig. 1** Absorption spectra of **1** (solid line), **2** (dotted line), and recovered **1** by annealing (broken line) in toluene. Note that the ordinate is arbitrary.

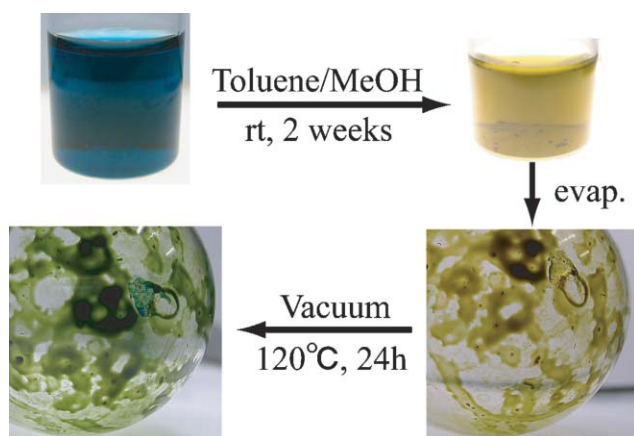
corresponding unsubstituted TAiBC. It is known that skeletal deviation causes a sizable bathochromic shift of the Q band of porphyrins and Pcs.<sup>9b,13</sup> The DFT (B3LYP/6-31G(d)) optimized structure also suggested a highly deformed aromatic core of **1** due to steric congestion of the adjacent phenyl groups (see Supporting Information†). Scheme 2 (top left) shows the color of a solution of **1** in toluene–methanol (1 : 4 (v/v)). The initial deep blue color, originating from  $\pi$ – $\pi^*$  transitions, changed to yellow on allowing the solution to stand for *ca.* 2 weeks at room temperature (Scheme 2, top right). In the case of TAC and TABC, colored solids precipitated after standing for 2 weeks. The presence of a radical trapping reagent (phenyl-*N*-*tert*-butyl nitrene) did not prevent the reaction. As shown in Fig. 1 (dotted line), the Q band disappeared completely, which indicates that the entire aromaticity of the macrocycle has been lost. X-ray quality single crystals of this unknown product were found on the bottom of the sample vessel. § Fig. 2 represents the ORTEP drawing of the yellow product. The structure was confirmed as **2**, that is, two methoxy groups are bound to the diagonal pyrrole  $\alpha$ -carbons of **1** (C4 and C12). The presence of  $sp^3$  carbons distorts the molecular skeleton significantly, and the conjugation order is halved. The C–O bond distances are 1.414(4) and 1.413(3) Å for O1–C4 and O2–C12, respectively. It is conceivable that one of the methoxy groups binds at the fused-benzene site (O2) so that the intramolecular stresses could be reduced. We are unsure whether the other methoxy group (O1) binds selectively on the same side of the molecular plane as



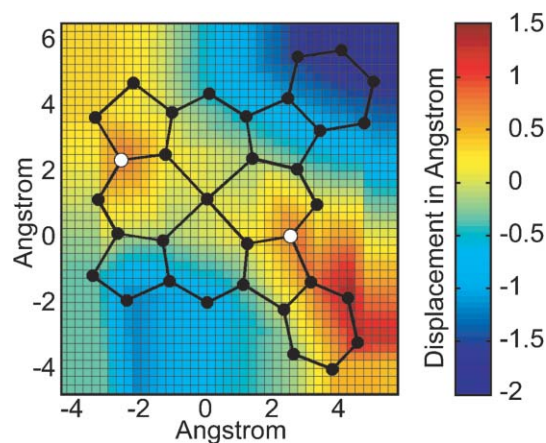
**Fig. 2** ORTEP representation of **2** (50% ellipsoids). Hydrogen atoms are omitted for clarity. Selected numbering system used in the analysis is depicted.

shown in the crystal structure, or that the *trans* isomer also exists in the solution. In order to compare the deformation mode with 14,28-(MeO)<sub>2</sub>NiPc, colormap analysis was performed.<sup>14</sup> As shown in Fig. 3, the four *meso*-nitrogens lie out of the 4N<sub>pyrrole</sub> plane, while the two fused benzene rings deviate either positively or negatively. This type of serpentine isogram is very similar to that obtained for 14,28-(MeO)<sub>2</sub>NiPc,<sup>14</sup> indicating that **2** is practically released from the phenyl–phenyl congestion. Compound **2** maintains the yellow color after evaporation of the solvent (Scheme 2, bottom right). However the color changed to green after annealing at 120 °C for 24 h (bottom left), and the absorption spectrum regained Q-band intensity (Fig. 1, broken line). Probably, the annealing induced a partial decomposition of **2**, and the formed by-products are responsible for the relatively large absorbance in the 300–500 nm region. This is why the recovered **1** appears green rather than the original blue. Taken together, the above data suggest that **1** and **2** reversibly transform between each other by choosing suitable reaction conditions (Scheme 1, top).

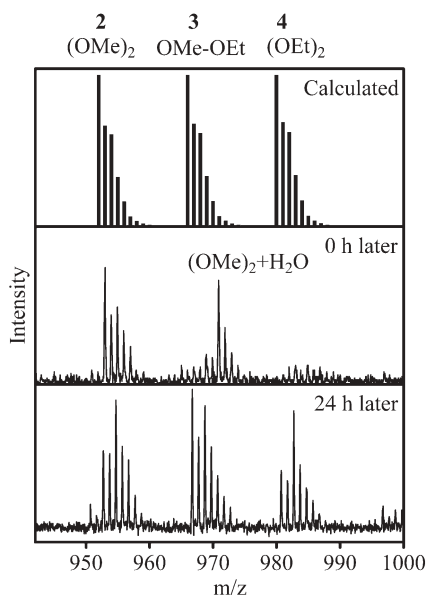
Compound **2** was also characterized by ESI-TOF-Mass spectrometry. The samples for the measurements were prepared by dissolving **2** in CHCl<sub>3</sub>–ethanol. Measurements were performed both immediately after and 24 h after sample preparation. The first



**Scheme 2** Color appearances in toluene–MeOH (1 : 4 (v/v)) (top) and in the solid state (bottom) for **1** (left) and **2** (right).



**Fig. 3** Colormap analysis of the crystal structures of **2**. Hydrogen atoms, and phenyl and methoxy groups are omitted for clarity. Hollow marks indicate  $sp^3$  carbons.



**Fig. 4** Calculated isotopic patterns for **2–4** (top). ESI-TOF mass spectra of **2** in  $\text{CHCl}_3$ –EtOH measured immediately after (middle) and 24 h after (bottom) sample preparation.

measurement detected molecular ion peaks at 952 amu, corresponding to **2**.<sup>15</sup> However, the second run clearly indicates the existence of methoxy-ethoxy (**3**) and bis-ethoxy (**4**) derivatives (966, 980 amu, respectively). Neither **3** nor **4** were detected in the first run (Fig. 4). Therefore, these are clearly formed not in the mass spectrometer, but in the sample solution during standing (Scheme 1, bottom).

In summary, we have found that the structurally stressed dibenzo-fused TAI<sub>3</sub>C derivative, **1**, reacts with methanol to give a bis-methoxy adduct, **2**, under very mild conditions. The color of **1** changes from deep blue to yellow as a result of the reaction. Furuta treated N-fused porphyrins with NaOMe–MeOH to give methoxy-substituted N-confused porphyrins.<sup>16</sup> Senge reported that treatment of metal-free tetra-*meso-tert*-butyl porphyrin with  $\text{HClO}_4$  and methanol yielded the *meso*-methoxy-substituted porphyrin (porphodimethene).<sup>17</sup> To our knowledge, however, this is the first example in which an aromatic Pc core reacts directly with an alcohol. Although further studies are necessary in order to determine the structural requirements of Pcs to induce this type of reaction, we suggest that the relatively high solubility of **1** in methanol is a likely reason.

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## Notes and references

† **1**: A mixture of 3,6-diphenylphthalonitrile (1.0 g, 3.6 mmol), tetramethylsuccinonitrile (780 mg, 5.73 mmol),  $\text{NiCl}_2$  (500 mg, 3.86 mmol) and

a catalytic amount of ammonium molybdate was refluxed for 2 h in quinoline under nitrogen. After cooling to room temperature, the reaction mixture was diluted with EtOH– $\text{H}_2\text{O}$  (1 : 1 v/v, 50 mL). The resulting precipitate was filtered, and washed with hot EtOH– $\text{H}_2\text{O}$  until the washings were colorless. The crude residue was passed through a short silica column ( $\text{CHCl}_3$ ) in order to remove polymeric by-products, and the obtained eluate was evaporated. A succession of extractions of the mixture with hexane and methanol followed by chromatographic separation (silica, toluene–cyclohexane (4 : 1 v/v)) gave the desired **1**. Spectral data: Mass (MALDI-TOF):  $m/z$  890 ( $\text{M}^+$ ); elemental analysis calcd for  $\text{C}_{56}\text{H}_{48}\text{N}_8\text{Ni}$ : C, 75.43; H, 5.43; N, 12.57; found: C, 73.33; H, 5.58; N, 11.60%. § Crystal data for **2**:  $\text{C}_{58}\text{H}_{54}\text{N}_8\text{NiO}_2$ ,  $M = 953.80$ ,  $a = 11.817(5)$ ,  $b = 15.359(6)$ ,  $c = 15.504(6)$  Å,  $\alpha = 73.82(2)$ ,  $\beta = 75.54(2)$ ,  $\gamma = 64.453(18)^\circ$ ,  $U = 2410.9(17)$  Å<sup>3</sup>,  $T = 223(2)$  K, space group  $P\bar{1}(\text{no. } 2)$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 0.456 \text{ mm}^{-1}$ , 18990 reflections collected, 8331 unique ( $R_{\text{int}} = 0.0257$ ),  $R_1 = 0.0534$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1215$  (all data). CCDC 283235. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512442e.

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