Molecular diabolos: synthesis of subphthalocyanine-based diboranes†

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Genuine B–B linked subphthalocyanine dimers are synthesized through Wurtz coupling of readily accessible chlorosubphthalocyanines.

Subphthalocyanines (SubPc's **1**, Fig. 1)[1,2] stand out among other structurally modified tetraazaporphyrins, because of their particular macrocyclic ring, formed by three isoindole subunits that are bound together by three aza-bridges. This unique make up gives rise to an aromatic 14 π-electron heteroannulene with specific characteristics, like the ability to accommodate a boron(III) ion within its central binding core. Indeed, subphthalocyanines are known only in the form of boron derivatives, and the metallomacrocycle ensemble possesses a conical shape, which is responsible for physical features like their octupolar character and hence, their extraordinary nonlinear optical properties.[3]

The physicochemical properties of these compounds can be fine-tuned by modifying the subphthalocyanine periphery through the introduction of a variety of functional groups[4] and by replacing the three isoindole subunits by three pyrrole rings, affording structurally related subporphyrazines (SubPz's).[5] Recently, related subporphyrins have also been reported.[6] Functionalization on the axial position is another approach to modulate the properties of these compounds and obtain tailored materials.[7] In this context, axially linked multimacrocyclic complexes may show enhanced properties or new ones, and therefore, we and others have reported two examples of subphthalocyanine μ-oxodimers [SubPcB–O–BSubPc] (**2**, Fig. 1).[8] In this communication, we wish to report the synthesis and characterization of novel "back-to-back" B–B-linked subphthalocyanine dimers [SubPcB–BSubPc] **3**.[9]

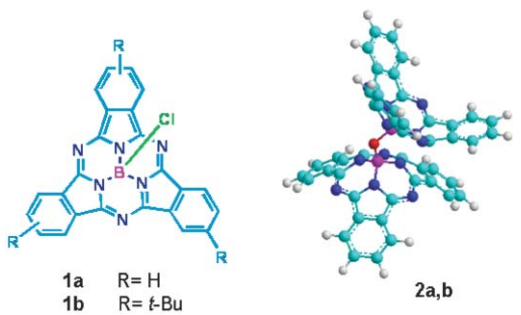

Fig. 1 Chlorosubphthalocyanines **1a,b**, and three-dimensional structure of reported subphthalocyanine μ-oxodimers **2a,b** (the R substituents have been omitted for clarity).

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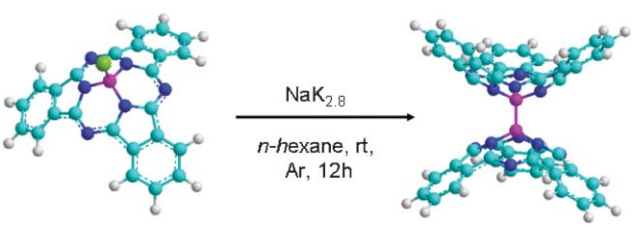
Focusing on the chemistry of boron, the very few reports on tetragonal N_n-bonded diboranes ($n \geqslant 4$) can be sorted into two classes, namely, dimeric tris(pyrazolyl)diborane derivatives[10] prepared by transamination reaction of tetrakis(dimethylamino)-diborane with appropriate pyrazoles, and a diborane(4) embedded within a porphyrin central cavity, attained through an intramolecular Wurtz coupling.[11] Subphthalocyanines carrying a halogen atom on the axial position[12] can be regarded as haloborane derivatives and bearing this in mind, we opted for the second synthetic pathway. Hence, the preparation of the subphthalocyanine diboranes **3a,b** (Scheme 1) was carried out by reductive coupling of the corresponding subphthalocyanine **1a,b** containing chlorine on the axial position, and using $NaK_{2.8}$ alloy as the reductive agent. The shape of the resulting subphthalocyanine dimers is very reminiscent of the Chinese "diabolo", and they are very labile and air-sensitive. Consequently, both the preparation and isolation of these diboranes were carried out under anaerobic conditions.

A common feature for all the subazaporphyrins that we have studied so far is constituted by their boron chemical shifts in ^{11}B NMR at −14 to −16 ppm.[8a] These low values arise from the boron type of coordination, which is tetragonal for all subazaporphyrins. Thus, the addition of a fourth ligand to the empty *p*-orbital of boron results in upfield chemical shifts with respect to the tricoordinated boranes.[13] The tetragonal diboranes **3a,b** also display upfield boron chemical shifts, but on going from the haloboranes **1a,b** to the diborane complexes **3a,b**, a significant change towards lower field is observed.[10c,11] Thus, compounds **3a,b** display in ^{11}B NMR broad signals (Figures S-2 and S-5), presumably due to the B–B couplings, at −1.1 and −0.6 ppm, respectively. This variation of *ca.* 14 ppm with respect to the monomers can be rationalized by taking into account the different strengths of the diverse kinds of coordination complexes, namely halo-, oxy- and diboranes. By applying the general rule, borane complexes endowed with a ligand containing a free electron pair, such as chloride or alkoxy, are found at higher field than the corresponding diboranes.[14]



Scheme 1 Synthesis of subphthalocyanine-based diboranes **3a,b**. The R substituents have been omitted for clarity.

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As expected, diboranes **3a,b** are very labile under the mass spectrometry conditions. Hence, the molecular ion corresponding to **3b** at m/z = 1125–1131 is very weak, the most intensive peak detected being the corresponding diborane half fragments $[M/2]^+$ and $[M/2 + H]^+$, centered at m/z = 563 and 564, respectively (Figure S-3). Fig. 2 shows the experimental isotopic pattern obtained for the molecular ion of compound **3b**, compared to the theoretical $[M + H]^+$ ion. The cluster actually consists of a mixture of $[M]^+$, $[M + H]^+$ and $[M + 2H]^+$. Likewise, the base peak for compound **3a** is centered at m/z = 395 and corresponds to the diborane half fragment $[M/2]^+$, while the molecular ion for this dimer is not detected. Other MS techniques like ESI-MS did not afford any significant peak.

^{1}H NMR spectroscopy provides additional structural information, in agreement with what is expected for diboranes **3a,b**. Hence, compound **3a** displays two multiplets at δ = 8.5 and 7.7 ppm corresponding to the aromatic fused benzene rings (see Figure S-4). These signals appear slightly shielded when compared to those exhibited by the precursor **1a** (Figure S-4), since in **3a** the protons fall under the influence of the other subphthalocyanine diamagnetic ring current, in the shielding cone. The effect is somewhat more pronounced ($\Delta\delta$ = 0.2 ppm) for protons located closer to the macrocyclic ring core, that are the benzene 3,6-positions. Interestingly, the phthalocyanine components of binuclear M–M linked phthalocyanine systems (M = In and Ga) have been reported not to fit into the other macrocycle ring-current cone.[15] On the contrary, the parallel μ-oxodimers **2a,b** display slightly shielded ^{1}H NMR chemical shifts, but in this case, the interaction between macrocycles may be favored due to their bent structure.[8a,b] In the case of the linear diboranes **3a,b** the diatropicity of one macrocycle does have a weak though detectable influence on the ^{1}H NMR spectrum of the other. It is likely that the differences observed between the distinct types of M–M linked dimers are related to the shorter B–B distances of *ca.* 1.7 Å reported for tetragonal diboranes,[10b,11] with respect to In–In (2.7–3.9 Å)[15b] and Ga–Ga (2.4–2.6 Å) interatomic distances.[15a] Shorter M–M distances should lead to closer macrocycles and consequently, more chances to interact with one another. Chlorosubphthalocyanine **1b** consists of a mixture of two structural isomers, *i.e.* C_1 and C_3, and hence, its ^{1}H NMR spectrum is more complicated, although three sets of signals, namely two aromatic and one aliphatic, are clearly distinguished.[8a] The ^{1}H NMR spectrum of the diborane **3b** (Figure S-1) maintains the same three groups of signals, but here the complexity is even higher due to the different isomeric combinations present in the dimeric diborane mixture. Again an upfield shift of ~1 ppm for aromatic signals, related to the chlorosubphthalocyanine **1b**,[8a] is observed.

The different bent and linear geometries of dimers **2a,b** and **3a,b**, respectively, are evidenced by UV/Vis spectrophotometry. Fig. 3 shows the electronic spectra of the subphthalocyanine diborane **3b**, the subphthalocyanine μ-oxodimer **2b**, and the chlorosubphthalocyanine precursor **1b**.

Usually, the axial ligands have little or no influence on the position of the subphthalocyanine B- and Q-bands. Likewise, the formation of a B–B bond to afford a subphthalocyanine diborane does not alter the main electronic characteristics of the macrocycles, and the absorption wavelengths are the same for precursors and products. Indeed, the only appreciable difference between the UV/Vis spectra of the monomers **1a,b** and the dimers **3a,b** is found in their molar extinction coefficients, those for diboranes being twofold those of the corresponding chloroboranes. Clearly, these values are directly related to the number of macrocyclic absorbers forming each system.

The lack of electronic communication between subphthalocyanine subunits in dimers **3a,b** denotes the σ character of the B–B bond and the rigidity of the system. Other structurally related M–M linked phthalocyanine dimers have also been reported to be electronically decoupled.[15] Besides, little or no mutual electronic

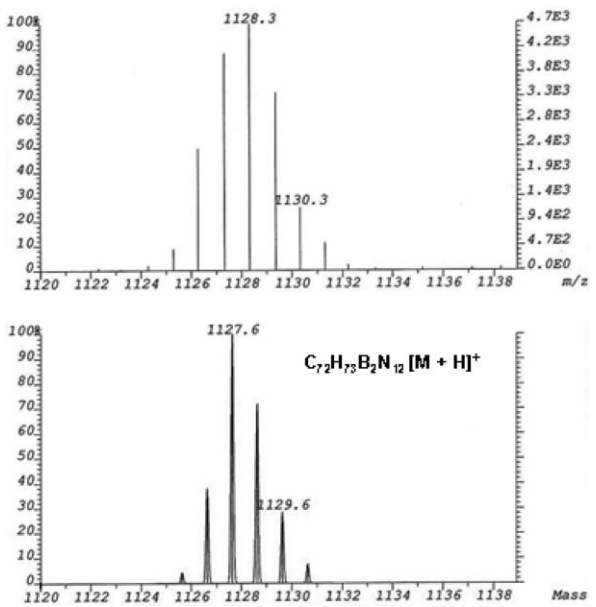

Fig. 2 Detail of isotopic pattern obtained by MS (FAB, *m*-NBA + TFA) for molecular ion of diborane **3b** and theoretical isotopic pattern for the corresponding $[M + H]^+$ ion.

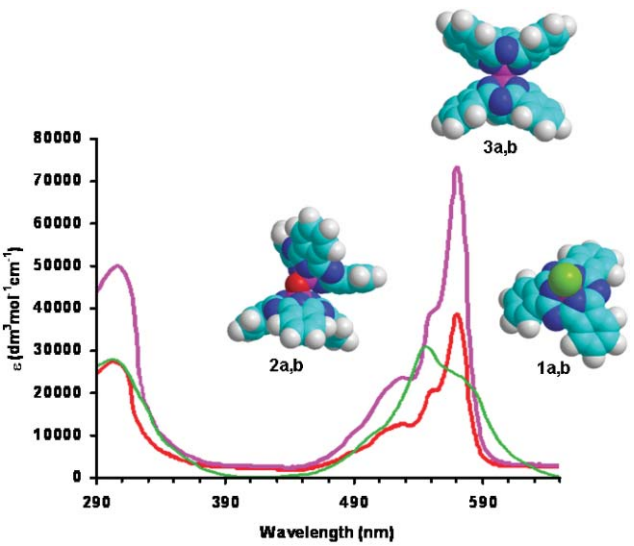

Fig. 3 UV/Vis spectra of **1b** (red line), **2b** (green line) and **3b** (pink line) in $CHCl_3$. Space filling representations of a chlorosubphthalocyanine (**1a,b**), a subphthalocyanine μ-oxodimer (**2a,b**) and a subphthalocyanine diborane (**3a,b**). Peripheral substituents have been omitted for clarity.

polarization of macrocycles must occur, otherwise it should be somewhat reflected by their electronic spectra. Figure S-8 shows the HOMO and the two types of degenerate LUMO MOs for subphthalocyanine **1a** and diborane **3a**.[16] No variation in the frontier orbitals is observed on going from the monomer to the dimer. Moreover, both HOMO and LUMO orbitals exhibit nodes at the boron atoms, this fact arguing for a lack of electronic communication between the two macrocycles in dimers **3a,b**. The presence of these nodes also explains the small to negligible effect of the axial substituents in the electronic spectra of subphthalocyanines and hence, the analogous UV/Vis spectra displayed by **1a,b** and **3a,b**.

The situation is drastically different for μ-oxodimers **2a,b**. Thus, the UV/Vis features of these compounds (Fig. 3) are characterized by a considerable blue shift and broadening of the chromophore Q-bands. Obviously, the changes observed with respect to the dimers **3a,b** arise from the different geometries of these two types of arrays. While diboranes **3a,b** are arranged in a linear and rigid manner, for dimers **2a,b** the geometry is determined by the angle defined by the two boron and the oxygen atoms (*ca.* 120°), which forces the two macrocycles to be in close proximity. The effect in the electronic spectrum is qualitatively comparable to that produced by the aggregation of phthalocyanines in solution.[17]

In conclusion, we have described for the first time the synthesis of genuine back-to-back B–B linked subphthalocyanine dimers *via* Wurtz coupling of readily accessible chlorosubphthalocyanines. Spectroscopic studies demonstrate that the two macrocyclic halves are electronically decoupled and provide evidence for a linear arrangement of the two subphthalocyanine subunits.

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