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Oligoyne-bridged boron subphthalocyanine dimers – synthesis and redox properties

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Dedicated to Professor Jan Bergman on the occasion of his 80th birthday

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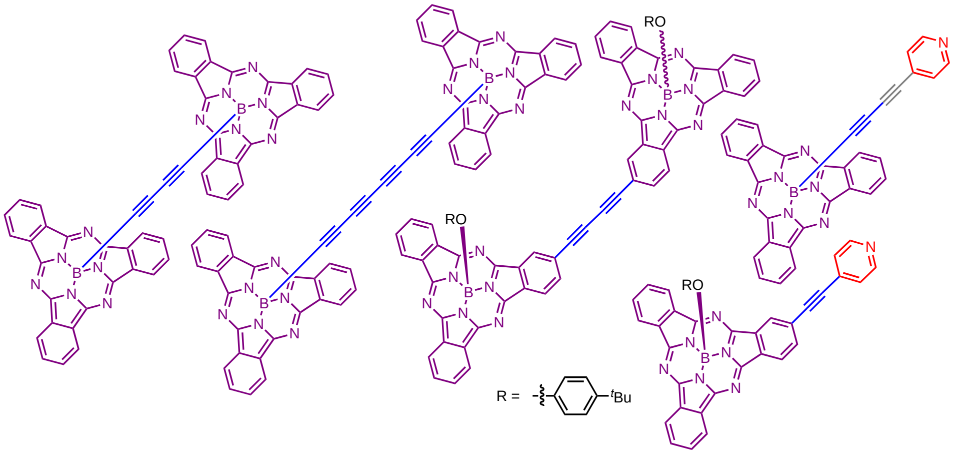
Abstract

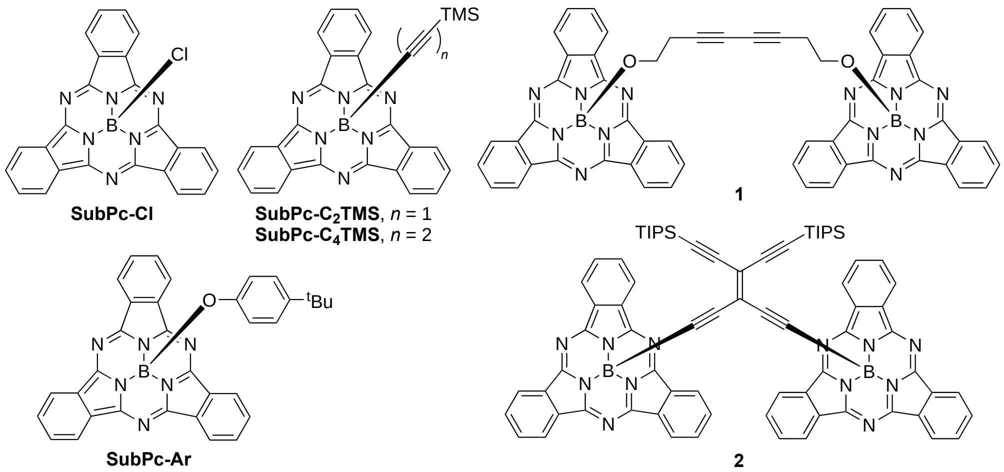
Here we present the synthesis and redox properties of a selection of boron subphthalocyanine dimers that are either connected by an oligoyne bridge via the axial boron atoms or via peripheral positions on the cyclic cores. The compounds were prepared by oxidative homodimerization reactions under Glaser-Hay conditions. Moreover, we show that the axial and peripheral terminal alkyne precursors can be subjected to Sonogashira coupling reactions, allowing the introduction of pyridyl end-groups.



Keywords: Alkynes, Glaser-Hay dimerization, oligoynes, redox centers, subphthalocyanine

Introduction

Boron subphthalocyanines are bowl-shaped macrocyclic molecules comprised of three aza-bridged isoindole units and a central boron atom with an axial substituent.[1] The simplest derivative, **SubPc-Cl** (Figure 1), having an axial chlorine substituent is prepared in one step from phthalonitrile and boron trichloride.[2] The axial chloride can easily be replaced by an alkoxy or phenoxy group[3] as in **SubPc-Ar**[4] or by a trimethylsilyl-protected alkynyl[5] as in **SubPc-C$_2$TMS** and **SubPc-C$_4$TMS**. SubPc derivatives are strong chromophores that in the absence of peripheral substituents have an absorption maximum similar to that of **SubPc-Ar** of 563 nm and an emission maximum around 573 nm in chloroform.[1,4] This class of dyes has in recent years found significant interest for organic light-emitting diodes, photovoltaics and photodynamic therapy applications.[6-16]



SubPc-Cl

SubPc-C$_2$TMS, *n* = 1
SubPc-C$_4$TMS, *n* = 2

1

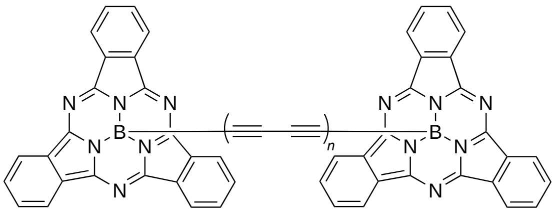
SubPc-Ar

2

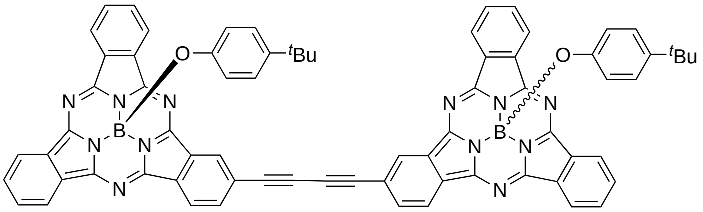
Figure 1. Known boron subphthalocyanine (SubPc) monomers and dimers.

SubPc's are also redox-active compounds. Thus, **SubPc-Ar** undergoes a reversible one-electron reduction at -1.56 V *vs* Fc/Fc$^+$ (Fc = ferrocene) to a radical anion and a further reduction to a reactive dianion at -2.05 V *vs* Fc/Fc$^+$.[4] It is oxidized to a reactive radical cation at +0.55 V *vs* Fc/Fc$^+$. Linking together two SubPc units by a flexible linker as in compound **1** resulted in two-electron reductions and oxidations at potentials similar to those of the monomer, signalling that the two units do not interact.[17] However, by bridging SubPc units by a tetraethynylethene bridge as in compound **2** some changes in redox properties were observed.[18] The two SubPc units were reduced in a reversible two-electron process at a potential of -1.57 V *vs* Fc/Fc$^+$; this potential is similar to that of the monomer, but the reduction peak was unusually sharp, which may indicate potential inversion where the monoanion is easier to reduce than the neutral precursor on account of an internal reorganization of the structure. Moreover, the oxidation of the two SubPc units was observed to occur sequentially at +0.54 V and +0.65 *vs* Fc/Fc$^+$, which indicates a Coulomb interaction between the two units.

We became interested in elucidating further the redox properties of SubPc dimers and here present the synthesis and properties of dimers **3**-**5** shown in Figure 2. The SubPc units of dimers **3** and **4** are connected via butadiynediyl and octatetraynediyl bridges at the axial boron atoms, while the units of dimer **5** are connected via a butadiynediyl bridge at periperal positions. Owing to the non-planarity of the SubPc unit, dimer **5** can exist as a meso isomer and a pair of enantiomers. In addition, we present the synthesis of acetylenic SubPc monomers containing a pyridyl end-group at either the axial or peripheral position, which may be employed as ligands for assembling SubPcs in metal complexes (yet to be explored in future work).



3, *n* = 1
4, *n* = 2

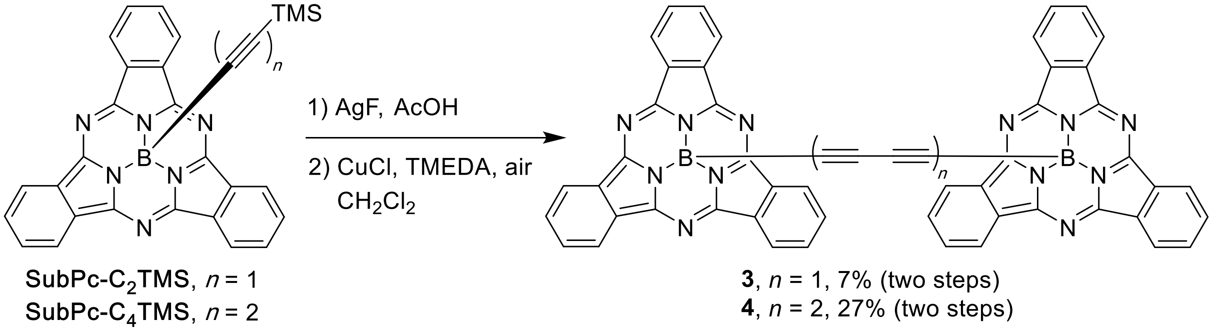


Meso/Racemic
5

Figure 2. New SubPc dimer target molecules.

Results and Discussion

Synthesis of dimers **3** and **4** proceeds according to Scheme 1. Treating the TMS-protected alkynes **SubPc-C$_2$TMS** and **SubPc-C$_4$TMS** with AgF and AcOH gave terminal alkynes that were subjected to oxidative Glaser-Hay dimerizations using CuCl, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) and oxygen from the air. The dimer **3** was only isolated in a yield 7% as it had to be subjected to several recrystallizations from a mixture of CH_2Cl_2, heptane and toluene before it was obtained in pure form. Purification of the dimer **4** was less tedious, and it was obtained pure in a yield of 27%. We managed to grow crystals of **3** from CH_2Cl_2, toluene and heptane that were subjected to X-ray crystallographic analysis (Figure 3). The quality of the data is somewhat poor (and there are disordered solvent molecules), but the data are at least good enough to confirm the structure. Structural confirmation of SubPcs often proves challenging when relying only on NMR spectroscopy due to missing carbon resonances[5,18,20] (as experienced also for the compounds included in this work). In ^{13}C NMR spectroscopic analysis, a dampening of signal intensity (as a result of broadening) for ^{13}C nuclei in vicinity of boron (^1J to ^4J) is observed, related to carbon-boron spin-spin coupling.[19] Hence inner sp^2-carbon atoms in the SubPc core as well as sp- and sp^2-carbon atoms at the axial substituent suffer from poor signal-to-noise ratios and are often very weak or not visible;[5,18,20] even with sensitive instrumental parameters.



Scheme 1

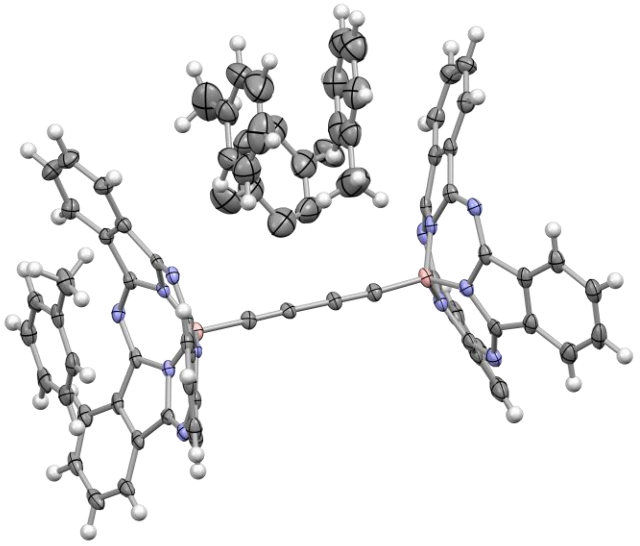
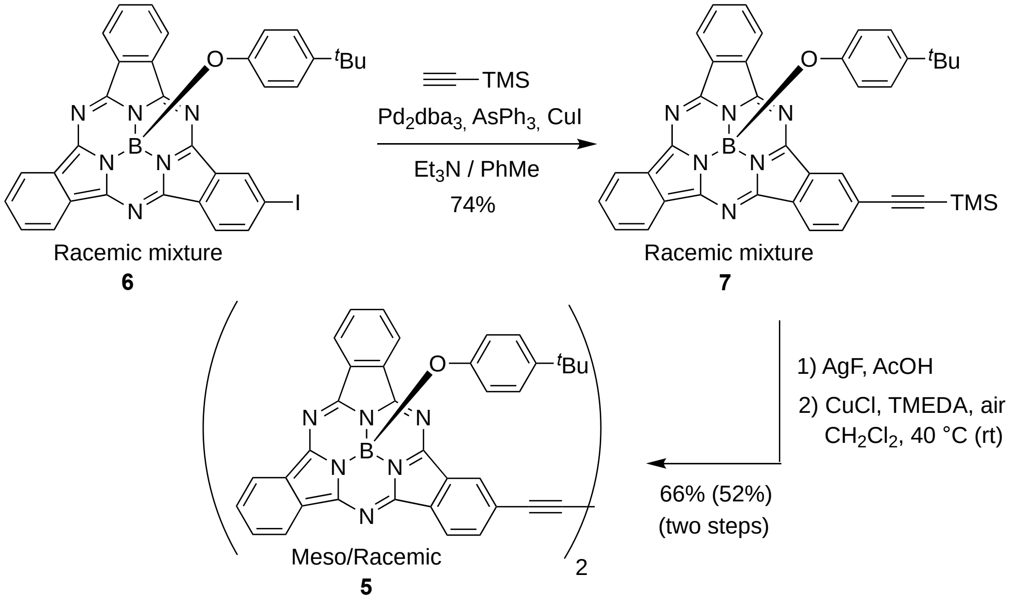


Figure 3. Molecular structure of **3** according to X-ray crystallographic analysis; disordered toluene molecules are also shown. CCDC 2006931.

Our next objective was to prepare the SubPc dimer **5**. Treating the known[20] iodo-functionalized SubPc **6** (racemic mixture) with trimethylsilylacetylene under Sonogashira conditions according to Scheme 2 gave compound **7** (racemic mixture). In this reaction, $AsPh_3$ was used as ligand instead of PPh_3 as we have previously[17] found this replacement advantageously for Sonogashira couplings involving SubPc substrates. Protodesilylation followed by oxidative Glaser-Hay dimerization in CH_2Cl_2 gave **5** in a good yield of 66% when performed at 40 °C and 52% when performed at room temperature (rt). This dimer was obtained as a diastereoisomeric mixture of a meso form and pair of enantiomers, which in our hands could not be separated by column chromatography.



Scheme 2

Analysis of the diastereoisomeric mixture of **5** by correlation spectroscopy revealed well-defined spin systems allowing assignment of all protons (Figure 4). For the non-substituted peripheral area (Spin systems 1 and 3), multiplet proton signals are observed. However, for the substituted peripheral vicinity (Spin system 2), three paired doublet of doublet signals are observed with internally related coupling constants of *J* 8.2, 1.4 and 0.8 Hz (Similar coupling patterns are also observed for the unsymmetrically substituted SubPc derivates **6**, **7** and **10**). The two diastereoisomers appear to be non-distinguishable by the NMR spectroscopic analysis. We note that there is no reason to believe that the relatively high-yielding synthesis should have provided only one of the diastereoisomers.

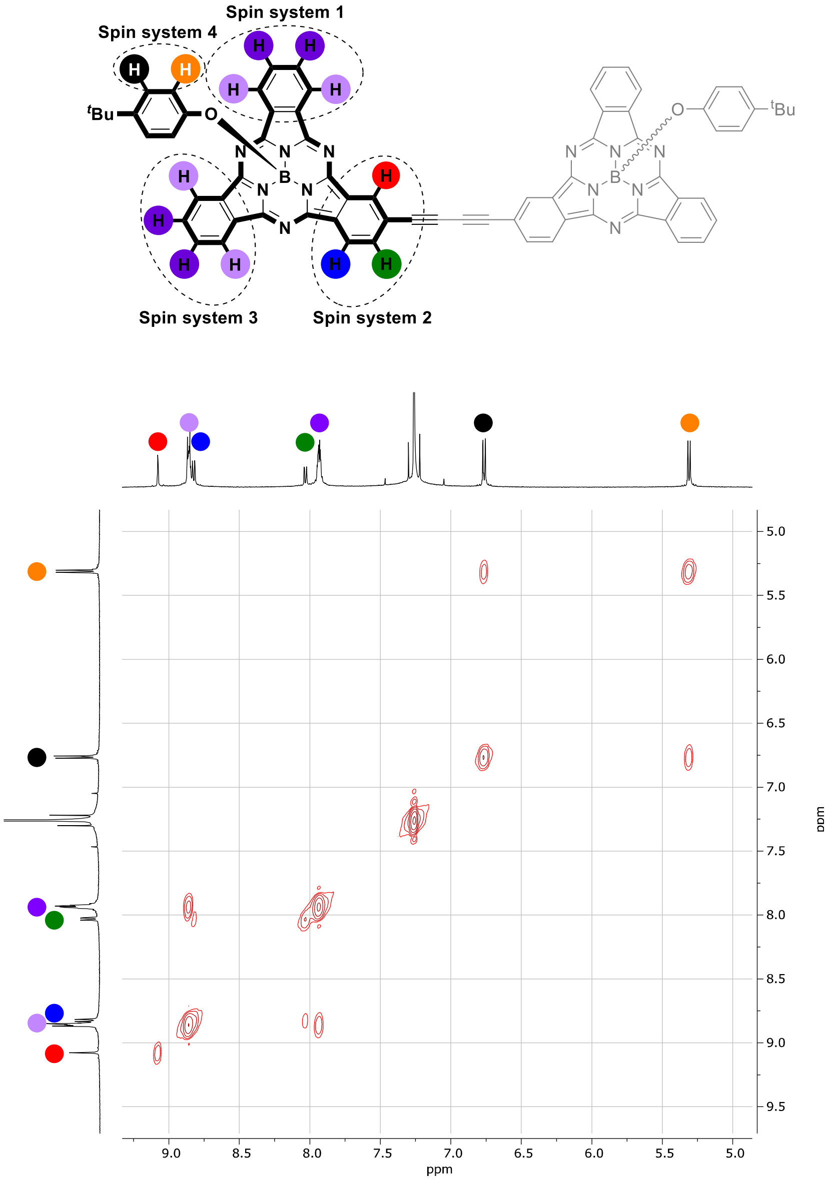
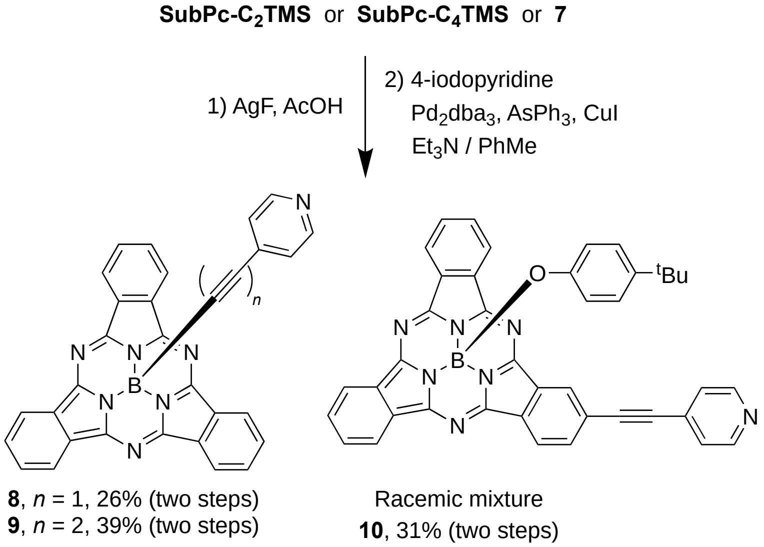


Figure 4. ^{1}H-^{1}H COSY (500 MHz, CDCl$_3$) spectrum of **5** (aromatic region selected) with assigned protons and spin systems. The *tert*-Butyl protons resonate at 1.08 ppm (not shown); see SI, Figure S6).

To explore further the possibility for coupling reactions with the SubPc's containing terminal alkynes, we subjected **SubPc-C$_2$TMS**, **SubPc-C$_4$TMS**, and **7** to desilylation followed by Sonogashira couplings with 4-iodopyridine to provide the products **8**-**10** shown in Scheme 3. In future studies, we will explore the pyridyl groups of these compounds as ligands for metal ions, which can be an alternative way of assembling two SubPc units.



Scheme 3

The UV-Vis absorption spectra of the three new dimers recorded in toluene are shown in Figure 5. Dimers **3** and **4** have longest-wavelength absorption maxima ($S_0 \rightarrow S_1$ Q band[1]) at 568 nm ($\varepsilon = 1.36 \times 10^5$ M^{-1} cm^{-1}) and 571 nm ($\varepsilon = 1.72 \times 10^5$ M^{-1} cm^{-1}), respectively, close to those of **SubPc-C$_2$TMS** (569 nm in CHCl$_3$; $\varepsilon = 8.91 \times 10^4$ M^{-1} cm^{-1}) and **SubPc-C$_4$TMS** (570 nm in CHCl$_3$; $\varepsilon = 8.53 \times 10^4$ M^{-1} cm^{-1}).[5] The intensities of these absorptions, however, seem to be less than twice those of the corresponding monomers. In contrast, dimer **5** exhibits a redshifted longest-wavelength absorption maximum at 593 nm ($\varepsilon = 1.74 \times 10^5$ M^{-1} cm^{-1}), in line with the fact that here a large conjugated π-system is present.

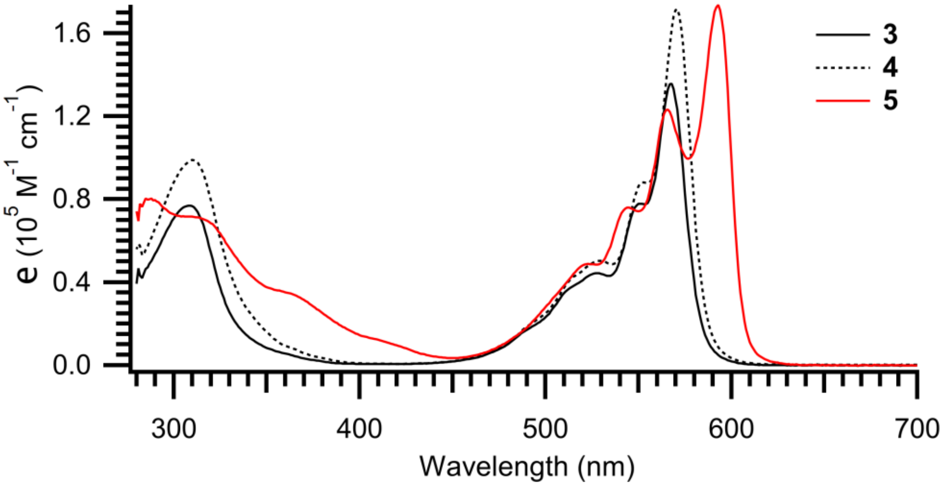


Figure 5. UV-Vis absorption spectra of dimers **3**-**5** in toluene.

The cyclic voltammograms (CVs) of dimers **3**-**5** are shown in Figure 6 together with the cyclic voltammogram of previously studied dimer **2**.[18] The voltammograms were recorded in CH_2Cl_2 using 0.1 M Bu_4NPF_6 as counter electrolyte, and potentials are referenced *vs* Fc/Fc^+ (the CV of ferrocene was recorded in a separate experiment). The Supplementary Material shows the corresponding differential pulse voltammograms (DPVs). Interestingly, the two oligoyne-bridged dimers **3** and **4** were significantly easier to reduce than the tetraethynylethene-bridged dimer **2**. Thus, from the differential pulse voltammograms we observe the first reductions at -1.51 V (**3**) and -1.49 V (**4**), while the first reduction of **2** was previously[18] reported at -1.57 V (all *vs* Fc/Fc^+). This observation may be explained by the fact that the rigid oligoyne bridges bring the two SubPc units further apart in comparison to the geminally substituted tetraethynylethene bridge (*i.e.*, less Coulomb repulsion). Thus, the boron-boron distance in dimer **3** is according to the X-ray crystal structure 6.99 Å, while the boron-boron distance in **2** was previously reported to 6.16 Å (based on X-ray crystallographic analysis). Yet, we have recently discovered that radical-stabilizing axial groups (to stabilize unpaired electron located on boron of the SubPc radical anion, while the negative charge is assumed to be delocalized within the macrocycle itself) and conjugated oligoynes render the reduction of SubPcs occur easier.[21] Thus, the stronger acceptor strengths of **3** and **4** may also relate to the linearly conjugated bridge separating the two boron centers in **3** and **4**, while the two boron centers are separated by a cross-conjugated bridge in **2**. In fact, dimers **3** and **4** are slightly easier to reduce than monomers **SubPc-C_2TMS** and **SubPc-C_4TMS** for which the first reduction occurs at -1.53 V *vs* Fc/Fc^+;[21] this easier reduction may relate to pairing of the unpaired electron on each boron (yet, the potential differences are quite small so one has to be careful in the interpretations). In contrast to **2**, the oxidations of **3** and **4** did not occur stepwise, but as a single peak in the DPV at +0.51 V (slightly broadened, however) for **3** and at +0.54 V for **4**. In comparison, monomers **SubPc-C_2TMS** and **SubPc-C_4TMS** are oxidized at 0.56 V and 0.58 V, respectively.[21] Dimer **5** where the cores of the two SubPc units are conjugated showed a reversible first reduction (-1.48 V from the DPV), close to that of dimers **3** and **4**, and a second quasi-reversible reduction (-1.93 V from the DPV). The oxidation of **5** was slightly more difficult than for the other dimers, occurring at +0.57 V.

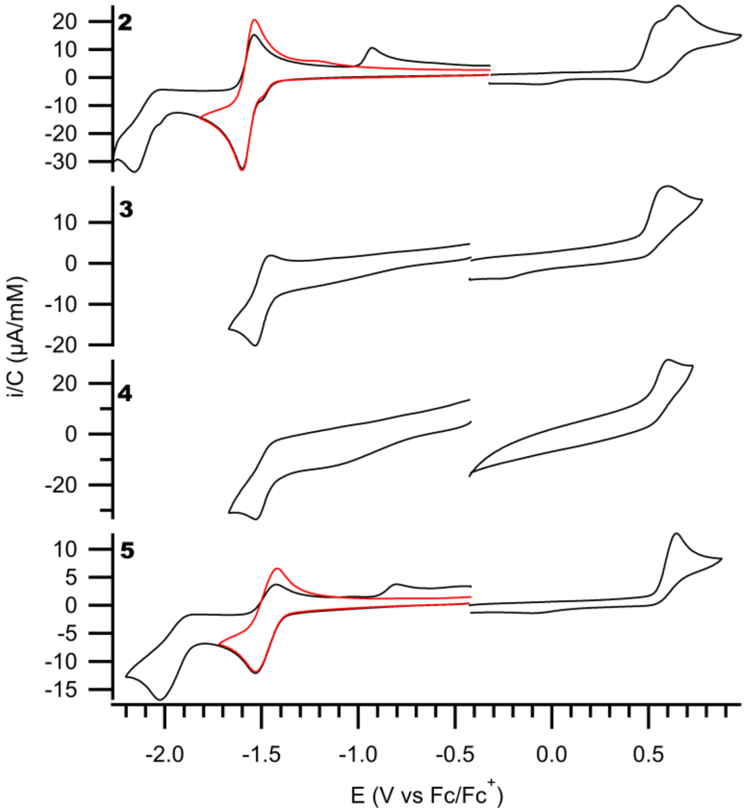


Figure 6. Cyclic voltammograms of dimers **2**-**5** in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6). Compounds **3** and **4** suffered from limited solubilites; hence the voltammograms of these were run at more dilute concentrations.

Conclusions

In summary, alkynylated SubPc derivatives were subjected to oxidative Glaser-Hay dimerizations, providing a selection of three new SubPc dimers. Dimerization by oligoyne bridges via the axial boron positions has little influence on the photophysical properties (dimers **3** and **4**), while dimerization via peripheral positions results in a redshifted longest-wavelength absorption (dimer **5**). The two SubPc units of the oligoyne-bridged dimers **3** and **4** were easier to reduce than the two units of the previously studied tetraethynylethene-bridged dimer **2**. This difference may be ascribed to a difference in geometries of these compounds (different degrees of Coulomb repulsions), but probably more likely to a larger degree of stabilization of an unpaired electron on each of the two boron atoms of the dianionic structure when the boron atoms are separated by linearly conjugated oligoyne bridges. To elucidate the subtle interactions that are in play, it could be interesting to subject the dianions to quantum-chemical calculations in the future.

Experimental Section

General. All reagents and solvents were obtained from commercial suppliers and used as received unless otherwise stated. The following compounds were prepared according to reported literature procedures: **SubPc-C$_2$TMS**, **SubPc-C$_4$TMS**[5] and **6**[20]. Purification by column chromatography was carried out on silica gel

(SiO_2, 60 Å, 40–63 µm). Thin-layer chromatography (TLC) was run on commercially available aluminum sheets pre-coated with silica gel and a fluorescence indicator and visualized under UV light (254 or 360 nm). NMR spectra were collected on a 500-MHz Bruker instrument with cryoprobe. Chemical shift values (δ) are quoted in ppm and coupling constants (J) in Hz. ^1H and ^{13}C NMR spectra are referenced to the deuterated solvent peak ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm). Mass spectrometry (HRMS) was performed using either Electrospray Ionization (ESI) or Matrix Assisted Laser Desorption Ionization (MALDI); FT-ICR = Fourier Transform Ion Cyclotron Resonance with dithranol as matrix. UV-Vis absorption measurements were collected on a Varian Cary 50 Bio UV-Visible Spectrometer (cuvette: 1 cm path length) in neat toluene. Cyclic voltammetry and differential pulse voltammetry were carried out using an Autolab PGSTAT12 instrument with Nova 1.11 software. All samples were analyzed in argon degassed dichloromethane solutions of 0.1 M tetrabutylammonium hexafluorophosphate at scan rates of 100 mV/s. A conventional three-electrode system was used - a glassy carbon disk (d = 3 mm) as the working electrode, a platinum wire as counter electrode and a silver wire as the reference electrode separated from the bulk solution by a ceramic frit. The potential of the reference electrode was determined versus ferrocene/ferrocenium (Fc/Fc^+) redox system. Melting points are not corrected.

Dimer 3. SubPc-C$_2$TMS (70 mg, 0.14 mmol) was dissolved in a solution of CH_2Cl_2 (9 mL) and AcOH (0.6 mL, 0.7 M in CH_2Cl_2), and then AgF (204 mg, 1.61 mmol) was added. The mixture was allowed to stir for 40 min, and then aqueous HCl (100 mL, 0.1 M) was added. The reaction mixture was vigorously stirred and extracted with CH_2Cl_2 (8 x 50 mL), the combined organic phases was dried over $MgSO_4$ and filtered. The volume was reduced to 50 mL and transferred to an open flask with 4Å molecular sieves (4.1 g). Then the catalyst system CuCl (79 mg, 0.80 mmol) and TMEDA (0.32mL, 2.1 mmol) was added in CH_2Cl_2 (2 mL). After stirring for 1.5 h, more catalyst was added, CuCl (77 mg, 0.78 mmol) and TMEDA (0.35mL, 2.3 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was allowed to stir for another 2 h. Then a third addition of catalyst, CuCl (82 mg, 0.83 mmol) and TMEDA (0.35mL, 2.3 mmol) in CH_2Cl_2 (2 mL), was added, and the mixture was stirred for another 20 h. The reaction mixture was passed through a plug of silica (eluent, toluene to EtOAc) twice. The remains were then recrystallized several times from a mixture of CH_2Cl_2, heptane and toluene, until a purple powder of the pure product **3** was obtained (4 mg, 7%). R_f = 0.26 (5% ethyl acetate/toluene). Mp > 230 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.71 (dd, *J* 5.9, 3.0 Hz, 6H), 7.81 (dd, *J* 5.9, 3.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.15, 130.80, 129.74, 122.12 ppm (2 signals missing). HRMS (MALDI +ve FT-ICR, dithranol) calcd for $C_{52}H_{24}B_2N_{12}$ $[(M)^{\cdot+}]$: *m/z* = 836.25001/837.24638/838.24275/839.24611; exp: *m/z* = 836.24807/837.24448/838.24068/839.24846; $C_{52}H_{25}B_2N_{12}$ $[(M+H)^+]$: *m/z* = 837.25784/ 838.25421/839.25058/840.25393; exp: *m/z* = 837.25612/838.25205/839.25590/840.25193.

Dimer 4. To a solution of **SubPc-C$_4$TMS** (108 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) were added AcOH (1 mL, 0.7 M in CH_2Cl_2) and AgF (267 mg, 2.10 mmol), and the reaction mixture was allowed to stir for 30 min. Then aqueous HCl (30 mL, 1 M) was added, and the biphasic mixture was allowed to stir for another 30 min. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (4 x 20 mL). The combined organic phases were dried over $MgSO_4$ and filtered, after which the solvent was reduced to 50 mL. Next, TMEDA (0.3 mL) and CuCl (62 mg, 0.63 mmol) were added, and the reaction mixture was allowed to stirr for 21 h in an open flask. After the reaction was done, more CH_2Cl_2 was added to fully dissolve the product, which was run through a plug of silica (gradient eluent, 50% CH_2Cl_2/toluene to toluene to 50% EtOAc/toluene). After removing the solvent under reduced pressure, the material was recrystallized from CH_2Cl_2/*n*-heptane to give the product **4** as a purple solid (25 mg, 27%). R_f = 0.26 (5% EtOAc /toluene). M.p. > 230 °C. ^1H NMR (500 MHz,

$CDCl_3$): *δ* = 8.80 (dd, *J* 5.9, 3.0 Hz, 12H), 7.87 (dd, *J* 5.9, 3.0 Hz, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 150.35, 130.90, 129.96, 122.28 ppm (4 signals missing). HRMS (MALDI +ve FT-ICR, dithranol) calcd. for $C_{56}H_{24}B_2N_{12}$ [(M)$^{\cdot+}$]: *m/z* = 885.24638/886.24275/887.24611, exp: *m/z* = 885.24538/ 886.25325/887.24960; $C_{56}H_{25}B_2N_{12}$ [(M)+H)$^+$]: *m/z* = 886.25421/887.25058/888.25393, exp: *m/z* = 886.25325/887.24960/888.25293.

Compound 7. An argon purged solution of Et_3N in toluene 1:3 (12 mL) was added to an argon purged reaction flask containing **6** (142 mg, 0.212 mmol), Pd_2dba_3 (39 mg, 0.43 µmol), CuI (8 mg, 0.04 µmol), and $AsPh_3$ (104 mg, 0.340 mmol). The flask was charged with trimethylsilylacetylene (1.17 mL, 8.47 mmol) and purged with argon for 2 min under sonication. The reaction mixture was stirred for 48 h, after which it was passed through a small plug of SiO_2 (eluent, 20% EtOAc/toluene), concentrated *in vacuo* and subjected to flash column chromatography (eluent, 20% EtOAc/heptane), which yielded the product **7** as a pink solid (101 mg, 74%). R_f = 0.33 (20% EtOAc/heptanes). Mp 185 – 186 °C. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 8.96 (dd, *J* 1.4 Hz, 0.8 Hz, 1H), 8.87 – 8.80 (m, 4H), 8.75 (dd, *J* 8.2 Hz, 0.8 Hz, 1H), 7.94 (dd, *J* 8.2 Hz, 1.4 Hz, 1H), 7.92 – 7.89 (m, 4H), 6.74 (d, *J* 8.8 Hz, 2H), 5.29 (d, *J* 8.8 Hz, 2H), 1.07 (s, 9H), 0.33 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 152.26, 151.76, 150.73, 150.12, 143.78, 132.91, 131.28, 131.16, 131.13, 130.81, 130.16, 130.15, 130.07, 129.99, 126.18, 125.83, 124.65, 122.43, 122.37, 122.35, 122.07, 117.83, 105.00, 97.42, 77.16, 33.96, 31.45, 0.09 ppm (5 signals missing). HRMS (MALDI +ve FT-ICR, dithranol) $C_{39}H_{34}BN_6OSi$ [(M)+H$^+$]: *m/z* = 641.26509, exp *m/z* = 641.26584.

Dimer 5. Method A. A solution of **7** (31 mg, 0.048 mmol) in CH_2Cl_2/MeCN 3:1 (4 mL) was charged with AgF (38 mg, 0.30 mmol) and AcOH in CH_2Cl_2 (0.5 mL, 0.7 M) and let to stir for 30 min. The reaction mixture was poured into aqueous HCl (50 mL, 0.05 M) and extracted with CH_2Cl_2, (3 x 50 mL), dried over $MgSO_4$, filtered on a sintered funnel (pore 3) and concentrated *in vacuo* to a volume of 10 mL. The concentrate was transferred to a smaller reaction flask, and CuCl (18.8 mg, 0.190 mmol) and TMEDA (0.06 mL, 0.40 mmol) were added. The reaction mixture was vigorously stirred in open flask at 40 °C for 45 min, filtered through a small plug SiO_2, (eluent, EtOAc), concentrated *in vacuo*, and subjected to flash column chromatography (eluent, 30% EtOAc/heptanes), which yielded a diastereomeric mixture of **5** as a purple solid (17 mg, 66%). *Method B:* A solution of **7** (32 mg, 0.050 mmol) in CH_2Cl_2/MeCN 3:1 (4 mL) was charged with AgF (32 mg, 0.25 mmol) and AcOH in CH_2Cl_2 (0.5 mL, 0.7 M) and let to stir for 30 min. The reaction mixture was poured into aqueous HCl (50 mL, 0.05 M) and extracted with CH_2Cl_2 (3 x 50 mL), dried over $MgSO_4$, filtered on a sintered funnel (pore 3) and concentrated *in vacuo* to a volume of 10 mL. The concentrate was transferred to a smaller reaction flask and CuCl (20 mg, 0.202 mmol), TMEDA (0.06 mL, 0.4 mmol) and mol. sieves (243 mg, 4Å) were added. The reaction mixture was vigorously stirred in open flask at rt for 45 min, filtered through a small plug SiO_2, eluted with EtOAc, dried over $MgSO_4$, concentrated *in vacuo* and subjected to flash column chromatography (SiO_2, 30% EtOAc/heptanes), which yielded a diastereomeric mixture of **5** as a purple solid (14.6 mg, 52%). R_f = 0.19 (30% EtOAc/heptanes). M.p. >230 °C. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 9.08 (dd, *J* 1.4 Hz, 0.8 Hz, 2H), 8.88 – 8.84 (m, 8H), 8.82 (dd, *J* 8.2 Hz, 0.8 Hz, 2H), 8.03 (dd, J 8.2 Hz, 1.4 Hz, 2H), 7.95 – 7.90 (m, 8H), 6.76 (d, *J* 8.8, 4H), 5.31 (d, *J* 8.8 Hz, 4H), 1.08 (s, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.75, 152.67, 151.95, 151.83, 150.29, 150.10, 143.86, 133.08, 131.39, 131.17, 131.15, 130.72, 130.34, 130.32, 130.19, 126.99, 125.88, 122.89, 122.51, 122.45, 122.41, 122.37, 117.85, 83.07, 76.48, 33.97, 31.46 ppm. HRMS (MALDI+ FT-ICR, dithranol) calcd. for $C_{72}H_{49}B_2N_{12}O_2$ [M + H$^+$]: *m/z* = 1135.42821, exp: *m/z* = 1135.42805.

Compound 8. SubPc-C$_2$TMS (151 mg, 0.305 mmol) was dissolved in CH_2Cl_2 (15 mL) by sonicating for 5 min. AcOH (1 mL, 0.7 M in CH_2Cl_2), MeCN (4 mL), and AgF (427 mg, 3.36 mmol) were added to the solution. After being stirred for 30 min, the mixture was subjected to an aqueous workup with HCl (200 mL, 0.05 M). The water phase was extracted with CH_2Cl_2 (10 x 50 mL) until the extracts were nearly colorless. The combined organic phase was dried over $MgSO_4$, concentrated *in vacuo* until some solvent still remained. Then toluene (20 mL) and Et_3N (6 mL) were added to the solution, and the mixture was purged with argon under sonication for 20 min. Then 4-iodopyridine (195 mg, 914 µmol), $Pd_2(dba)_3$ (61 mg, 0.067 mmol), $AsPh_3$ (196 mg, 0.64 mmol), and CuI (51 mg, 0.27 mmol) were added to the solution. After stirring for 19 h under argon, the reaction mixture was passed through a short plug of silica (eluent, 50% EtOAc/toluene). The remains were then subjected to flash column chromatography (SiO_2, 20:80 EtOAc/toluene), giving the product **8** (40 mg, 26%) as a purple solid. R_f = 0.28 (20% EtOAc/heptane). M.p. > 260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.88 (dd, *J* 5.9, 3.0 Hz, 6H), 8.20 (dd, *J* 4.5, 1.6 Hz, 2H), 7.92 (dd, *J* 5.9, 3.0 Hz, 6H), 6.61 (d, *J* 4.5, 1.6 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ= 150.60, 131.02, 129.97, 125.60, 122.32 ppm (4 signals missing). HRMS (ESP) calcd for $C_{31}H_{17}BN_7^+$ [M+H$^+$] : *m/z* = 497.16693/498.16330/499.16666, exp *m/z* = 497.16626/498.16259/499.16597.

Compound 9. SubPc-C$_4$TMS (83.3 mg, 0.166 mmol) was dissolved in CH_2Cl_2 (5 mL) by sonication for 8 min. Subsequently AcOH (0.5 mL, 0.7 M in CH_2Cl_2), MeCN (2 mL), and AgF (213 mg, 1.68 mmol) were added to the solution. After being stirred for 1 h, the solution was subjected to an aqueous workup with HCl (150 mL, 0.05 M). The water phase was extracted several times with CH_2Cl_2 (6 x 50 mL). The combined organic extracts was dried over $MgSO_4$ and concentrated until some CH_2Cl_2 was still present. Then toluene (20 mL) was added, and the volume was reduced to 10 mL *in vacuo*. Then Et_3N (3 mL) was added to the solution, and the mixture was purged with argon while being sonicated for 20 min. Next 4-iodopyridine (97.8 mg, 0.498 mmol), $Pd_2(dba)_3$ (31 mg, 0.034 mol), $AsPh_3$ (97 mg, 0.32 mol), and CuI (26 mg, 0.14 mmol) were added to the solution. After stirring for 19 h under argon, the reaction mixture was passed through a short plug of silica (eluent, 50% EtOAc/toluene). The residue was then subjected to flash column chromatography (eluent, 20 % EtOAc/toluene), giving the product **9** (34 mg, 39%) as a purple solid. R_f = 0.22 (20% EtOAc/Toluene). M.p. > 260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ= 8.87 (dd, *J* 5.9, 3.0 Hz, 6H), 8.40 (br s, 2H), 7.91 (dd, *J* 5.9, 3.0 Hz, 6H), 6.97 (apparent d, *J* 4.9 2H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ= 150.49, 149.71, 130.99, 130.02, 129.76 122.33, 77.91, 72.30 ppm (3 signals missing). HRMS (ESP) calcd. for $C_{33}H_{17}BN_7^+$ [M+H$^+$]: *m/z* = 521.16693/522.16330/523.16666, exp: *m/z* = 521.16564/522.16192/523.16529.

Compound 10. A suspension of **7** (48 mg, 0.075 mmol) and CH_2Cl_2 (10 mL) was sonicated for 10 min under argon. Then AcOH (1 mL, 0.7 M in CH_2Cl_2) and AgF (76.3 mg, 0.60 mmol) were added to the mixture, which then was stirred for 1.5 h at ambient temperature under argon. Then a further portion of AgF (28.9 mg, 0.23 mmol) was added due to the presence of starting material, determined by TLC (eluent, 20% EtOAc/Heptane). After 1 h of further stirring, no more starting material could be observed on TLC. The reaction was stopped by addition of aqueous HCl (100 mL, 0.1 M); the mixture was transferred to a separation funnel with CH_2Cl_2 (50 mL). The biphasic mixture was separated and the aqueous phase was extracted with CH_2Cl_2 (6 x 50 mL). The combined organic phases were dried over $MgSO_4$ and the drying agent was filtered off. Toluene (40 mL) was added to the solution and CH_2Cl_2 was removed under reduced pressure to leave the deprotected alkyne in a toluene solution. Next 4-Iodopyridine (65 mg, 0.32 mmol), and Et_3N (5 mL) were added to the solution, which then was purged with argon. Subsequently Pd_2dba_3 (11.6 mg, 0.012 mmol), CuI (2.2 mg, 9 µmol), and $AsPh_3$ (20.2 mg, 0.064 mmol) were added. The reaction mixture was stirred under argon for 15 hours (TLC eluent: 50% EtOAc/Heptane). The reaction was quenched with water (100 mL). The phases were separated, and the water phase was extracted with toluene (4 x 40 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (gradient elution, 35–50% EtOAc/Heptane), then a second purification by flash column chromatography (eluent, 45% EtOAc/Heptane) to give **10** as a purple solid (31% yield). R_f = 0.30 (45% EtOAc/Heptane). M.p.= 224 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.06 (apparent triplet, *J* 1.0 Hz, 1H), 8.82 – 8.86 (m, 5H), 8.68 – 8.67 (m, 2H), 8.01 (dd, *J* 8.2, 1.3 Hz, 1H), 7.90 – 7.92 (m, 4H), 7.47 (d, *J* 4.6 Hz, 2H), 6.76 (dd, *J* 6.6, 2.1 Hz, 2H), 5.31 (dd, *J* 6.6, 1.1 Hz, 1H), 1.08 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.65, 152.61, 151.88, 151.84, 150.39, 150.36, 150.10, 150.01, 143.87, 132.56, 131.37, 131.35, 131.33, 131.16, 131.13, 130.80, 130.37, 130.30, 130.29, 130.18, 130.16, 126.22, 125.87, 125.76, 123.32, 122.50, 122.39, 122.37, 117.83, 94.12, 89.04, 33.97, 31.45 ppm (2 signals missing). HRMS (ESP) calcd for $C_{41}H_{29}BN_7O^+$ [M+H$^+$]: *m/z* = 646.2521, exp: *m/z* = 646.2520.

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Supplementary Material

NMR spectra, UV-Vis absorption spectra and electrochemical data.

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