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Subphthalocyanine–Dehydro[18]annulenes

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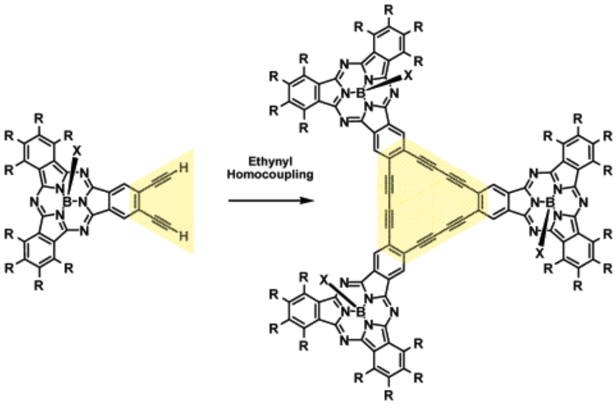
ABSTRACT



A subphthalocyanine trimer built around a dehydro[18]annulene core was prepared. The synthesis was achieved through direct homocoupling of an *ortho*-diethynyl-functionalized subphthalocyanine, obtained by palladium-catalyzed cross-coupling of the corresponding diiodo-subphthalocyanine with an ethynyl derivative. The lower analogue dehydro[12]annulene did not form in these homocoupling conditions. The trimers were fully characterized and their electrochemical properties investigated.

The use of ethynyl functional groups in carbon−carbon coupling strategies has been widely disseminated and consolidated as a reliable tool in the preparation of oligomeric arrays of porphyrins,[1] phthalocyanines,[2] and related macrocycles. Such arrays have been investigated in the last decades, aiming at the extension of the chromophore conjugation, thus shifting the visible absorption band to the infrared or near-infrared regions. These extended conjugated systems may find applications such as sensitizers for photovoltaic devices, photodynamic therapies, and printing technologies.[3]

In this sense, donor/acceptor dehydro[18]annulenes[4] have attracted special interest for the construction of highly conjugated optoelectronic materials and have been fused to different electroactive units such as *p*-benzoquinones[5] and tetrathiafulvalenes.[6] Phthalocyanines[7] have also been used in the preparation of ethynyl-linked dimers and dehydro-

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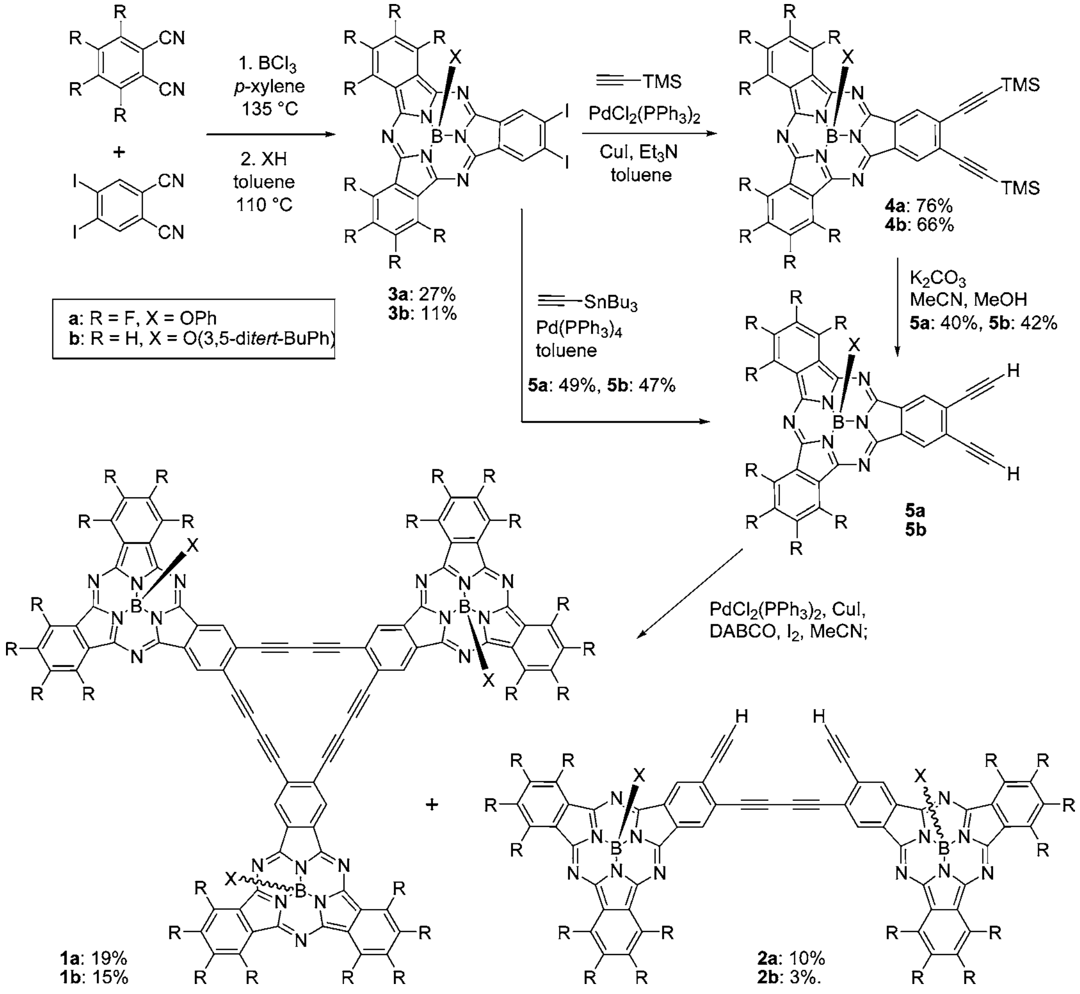
Scheme 1. Synthesis of SubPc−Dehydro[18]annulene Trimers **1a,b**



annulene dimers and trimers.[8] However, similar compounds employing subphthalocyanines (SubPcs),[9] which are lower analogues of phthalocyanines composed of three isoindole units N-fused around a boron atom, have not been reported so far. Subphthalocyanines are nonplanar aromatic molecules that show very attractive photophysical and electrochemical properties with applications as chromophores in nonlinear optics,[10] in OLEDs,[11] in photovoltaic devices,[12] and in multicomponent donor−acceptor systems.[13]

Here we describe the preparation of the first subphthalocyanine−dehydro[18]annulene structures. The synthetic pathway for the construction of these compounds is depicted in Scheme 1. In order to get a better idea of the scope of subphthalocyanine reactivity, the synthetic route was carried out starting from two differently substituted nonsymmetric SubPcs (**3a** and **3b**). The reduced solubility of unsubstituted subphthalocyanines (**b**) was counterbalanced by axial substitution with a di-*tert*-butylphenoxy group.

Diiodo-subphthalocyanines **3a** and **3b** were prepared in 27 and 11% yields, respectively, by statistical condensation

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of 4,5-diiodophthalonitrile and tetrafluorophthalonitrile or phthalonitrile, respectively, in the presence of BCl_3 in *p*-xylene, followed by substitution of the axial chlorine atom by phenol and 3,5-di-*tert*-butylphenol, respectively. In order to maximize the formation of these particular diiodosubphthalocyanines **3a** and **3b** with respect to other unsymmetrically substituted subphthalocyanines statistically produced in the course of the reaction as side compounds, the optimal phthalonitrile/diiodophthalonitrile ratio employed was 3.5:1 for **3a** and 3:1 for **3b**. Yields for the **b** series are somewhat lower, due to the relative poor reactivity of the unsubstituted phthalonitrile.

In a first approach, diethynyl-functionalized SubPcs **5a** and **5b** were synthesized in a two-step procedure. In the first step, SubPcs **4a** and **4b** were obtained in 76 and 66% yields, respectively, by palladium-catalyzed Sonogashira cross-coupling reaction between trimethylsilyl-protected acetylene and SubPcs **3a** and **3b**, respectively. In the second step, removal of the TMS protecting group in basic or nucleophilic conditions gave rise to SubPcs **5a** and **5b** in 40 and 42% yields, respectively. Due to the reduced yields obtained in the deprotection step (usually a quantitative procedure), an alternative single-step Stille cross-coupling reaction using ethynyltributylstannane was attempted and achieved in better yields (47 and 49% yield in one step for **5a** and **5b**, respectively). Under these conditions, significant amounts of Sonogashira cross-coupling byproducts (coupling of the terminal side of the triple bond of ethynyltributylstannane to the corresponding iodosubphthalocyanine) could be isolated.[14] The butyltin appendages could be easily removed quantitatively in acidic media, recovering more of the desired products **5a** and **5b**.

Formation of the dehydroannulene trimers **1a** and **1b** by homocoupling reactions of diethynyl-SubPcs **5a** and **5b** could not be achieved using classical conditions such as the Glaser, Eglington (copper salts and pyridine), or Hay (copper chloride and TMEDA) conditions since the strong nucleophilic media employed in these methods produced ring opening of the subphthalocyanines in a few minutes.[15] Instead, milder palladium-catalyzed methods in an oxidative environment were used.[16] These procedures still require small amounts of nucleophiles (in order to form the acetylides), which gave rise to a significant amount of decomposition, resulting in trimers **1a** and **1b** in 19 and 15% yields, respectively. Optimization of the reaction conditions was attempted by modification of several parameters, such as the nature of the catalyst ($Pd(OAc)_2$ or $PdCl_2(PPh_3)_2$) and its amount (2−15%), as well as the cocatalyst (CuI) and nucleophile (DABCO) proportions, 3−30% and 1−3 equiv, respectively. Different reoxidants were tested (O_2 and I_2) as well,[17] and reaction time was varied ranging from 2 to 24 h. Best conditions are shown in Scheme 1. A dehydro[12]-annulene dimer was also expected as product of the homocoupling reaction, but it was not detected. Instead, we isolated the related open diethynyl-linked SubPc dimers **2a** and **2b** in 10 and 3% yields, respectively.

Compounds **1a** and **1b** should be in fact a mixture of two topoisomers—one with all SubPc units facing the same direction, and another with one of the SubPc moieties facing the opposite direction. However, these isomers were neither isolated nor differentiated from the characterization data. From ^1H NMR spectra, it was possible to confirm unambiguously the existence of a closed annulene moiety in compounds **1a** and **1b**, as only one signal is observed for the two SubPc protons vicinal to the ethynyl groups at 9.25 ppm. Likewise, the dimers **2a** and **2b** were proved to be open structures, with the observation of two signals for these protons (9.04 and 9.11 ppm), as well as the appearance of a signal corresponding to the terminal alkyne protons at 3.73 ppm (see Supporting Information).

The UV−vis spectra of SubPcs **1**−**5** exhibit a B or Soret band at ca. 320 nm and a Q band in the visible region. The Q band absorption maximum undergoes a stepwise bathochromic shift on going from a single-unit SubPc (compound **5**) to the SubPc−dehydroannulene trimer (**1**), by ca. 20 nm per SubPc unit (Figure 1). Extinction coefficients also increase in the same order, as expected from the presence of increasingly larger π surfaces.

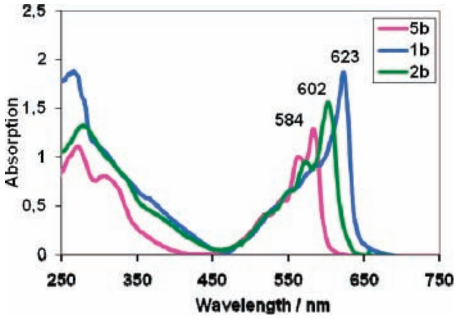

Figure 1. UV−vis absorption spectra of compounds **1b**, **2b**, and **5b**.

Subphthalocyanine derivatives **1**−**5** have π-amphoteric properties, exhibiting several reduction processes, with only the first one being chemically reversible, and an irreversible oxidation process.[18] Cyclic voltammetry data in THF (see Supporting Information for experimental details) are collected in Table 1. SubPcs **3a** and **5a** present a first reduction process at −1083 and −1081 mV, respectively. The two SubPcs

Table 1. Redox Potentials Obtained from Cyclic Voltammetry for Compounds **1a**, **3a**, and **5a** (THF, in mV versus Fc/Fc^+)

compound	E^1_{ox}[a]	$E^1_{1/2,red}$
3a	+926	−1083
5a	+911	−1081
1a	+880	−1027

[a] Irreversible oxidative processes; only anodic peak potentials are reported.

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(14) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004.

exhibit also an irreversible oxidation process at +926 and +911 mV, respectively (Figure 2). The incorporation of two acetylenic units at the periphery of SubPc **5a** results in a small improvement of both redox processes.

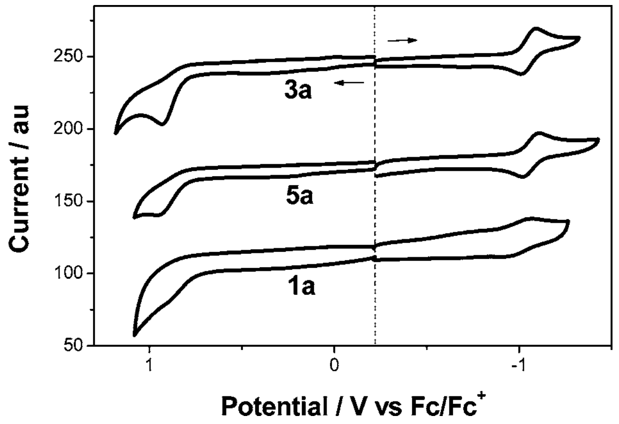

Figure 2. Cyclic voltammograms of compounds **1a**, **3a**, and **5a**.

Likewise, the SubPc−dehydroannulene trimer **1a** presents several reduction processes, with only a reversible couple at −1027 mV. However, this first reduction process is anodically shifted relative to **5a** by 50 mV. In oxidative scans, an irreversible process is observed at +880 mV, cathodically shifted by 30 mV relative to **5a**. These results substantiate easier redox processes for the subphthalocyanine−dehydro[18]annulene **1a** when compared to those of monomeric subphthalocyanines **5a** and **3a** due to the extension of conjugation.

In summary, new electroactive tris(subphthalocyanine) dodecadehydro[18]annulenes have been synthesized and fully characterized. The electronic properties of the trimers, investigated by both UV/vis absorption spectroscopy and electrochemistry, evidenced the formation of conjugated π-electronic extended subphthalocyanines.

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Supporting Information Available: Experimental procedures and full characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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