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Phthalocyanine-boronates: a synthon for the preparation of molecular assemblies

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ABSTRACT

Covalently linked phthalocyanine–phthalocyanine (Pc–Pc) heterodimers and Pc–Pc triad phthalocyanines connected through phenyl–phenyl (C–C) linkages are prepared using phthalocyanine-boronate (Suzuki Pc-synthon) and palladium catalyst.

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Carbon–carbon bond forming reactions are key steps in the preparation of complex bioactive molecules. Such reactions are also vital in developing libraries of organic materials with novel electronic, optical or mechanical properties. The most important carbon–carbon bond-forming methodologies use transition metals to mediate the reaction in a controlled and selective manner.[1] Among these, the cross-coupling reaction of organoboron compounds (Suzuki synthons) with organic electrophiles catalyzed by a palladium (Pd) complex is most widely used.[2] Such synthons are nontoxic, react under a variety of conditions (including aqueous), and exhibit air- and water-stability. The inorganic boron by-products are easily removed upon completion of the reaction. The coupling proceeds with high regio- and stereoselectivity, is little affected by steric hindrance and does not affect other functional groups in the molecule.

Phthalocyanines (Pc) and related tetrapyrrolic macrocycles have many interesting properties with applications in numerous important technological fields.[3] Many methods have been developed to modify Pc in order to improve their effectiveness for selected applications. Pd-catalyzed coupling reactions of Pc using halogenated Pc templates provide an interesting route to synthesize new families of unusually elaborated Pc macrocycles.[4] A few examples of Suzuki coupling reactions using halogenated Pc and arylboronic acid have been reported.[5] However, the use of Pc-boronate as a synthon for such coupling reactions has not previously been studied. Here, we describe the synthesis of Pc-boronate and evaluated its use as a synthon for the Suzuki coupling reaction with various arylhalides. The procedure allows for the synthesis of novel unsymmetrical Pc–Pc hetero-dimers and Pc-based branched triad, that is, Pc–$(Pc)_2$. Among different approaches to prepare arylboronates, the Pd-catalyzed cross coupling reaction between boronate and arylhalide is a convenient method. Pinacolborane and bis(pinalcolato) diborane are the most widely used for such reactions.

For our initial attempt to prepare Pc-boronate, we used a reported method[6] involving pinacolborane and monoiodo tri-*t*-butyl zinc phthalocyanine (**1**);[5a,7] however, this reaction failed to provide the desired product. Alternatively, using bis(pinalcolato)diboronate and **1** in DMF under argon for 2 h at 90 °C with $PdCl_2$(dppf) as catalyst and potassium acetate as base, coupling proceeded smoothly.[8] After purification, the Pc-boronate **2** was obtained in >70% yield (Fig. 1). The assigned structure was confirmed by spectral analysis: MS, MALDI-TOF (*m/z* 870), and characteristic UV–vis

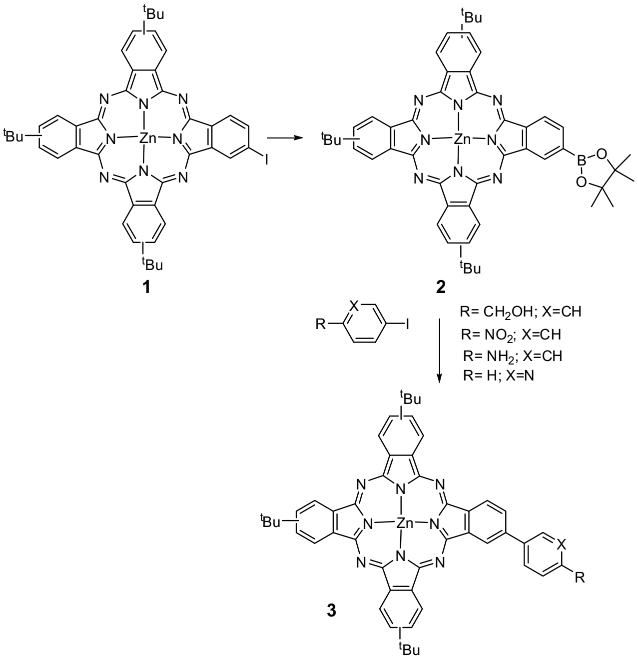

Figure 1. Synthesis of Pc-borane synthon and its reaction with aryl halides.

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absorption Q band at λ_{max} 674 nm. The Pc-pinacol boronate **2** is quite stable and can be kept for a long time in the dark without decomposition. The Pc-pinacol boronate **2** consists of regioisomers due to the parent monomers **1**.

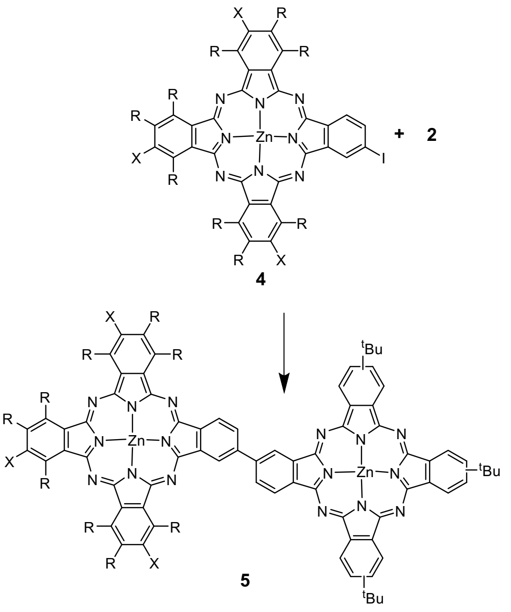
The utility of the Pc-synthon **2** is exemplified in Suzuki type cross coupling reactions as presented in Figure 1. The coupling reaction of **2** with a number of substituted arylhalides in DMF under argon at 90 °C using $PdCl_2$(dppf) as catalyst and 2% aqueous sodium carbonate for 2 h proceeded smoothly and the products **3** were isolated in 70–80% yield. Under the same conditions, using 3-bromopyride, the reaction proceeded sluggishly and the product was obtained in low yield (30%). A variety of arylhalides bearing electron-withdrawing or electron-donating substituents can be used in this cross-coupling reaction. MS analysis of all coupling products gave the expected molecular ion and characteristic UV–vis absorption Q-band maxima.

Recently, we reported a Pd-catalyzed coupling reaction using Pc–I monomers for the synthesis of covalently linked Pc–Pc homo-dimers connected through a C–C linkage of the benzene rings.[9] In all cases, reduced Pc was formed as a secondary, or even major product. Synthesis of Pc–Pc hetero-dimers using this approach requires two different Pc–I monomers resulting in complex reaction mixtures of both homo- and hetero-dimers and reduced Pc of either monomer. Furthermore, different homo-dimers require different coupling reaction conditions. On such account, we investigated the use of the Pc-boronate **2** as a Suzuki synthon for the synthesis of Pc–Pc hetero-dimers.

This new approach involves coupling Pc-boronate **2** to substituted monoiodo-Pc **4** (Fig. 2). Among the ligands that have been reported for the Suzuki–Miyara coupling reaction, 2-(2,6-dimethoxybiphenyl)-dicyclohexylphosphine (S-Phos) gave good to excellent yield.[10] The Pc-borane complex **2** and mono-iodo tri-dodecakis(2,2,2-trifluoroethoxy)ZnPc (**4a**)[11] (1:1.1 molar ratio) were dissolved in toluene under nitrogen, catalyst tris(dibenylideneacetone)dipalladium (Pd_2dba_3) was added together with ligand S-Phos and K_3PO_4 as a base, and the mixture was heated at 90 °C for 3h. Purification of the reaction mixture by silica gel column chromatography and analysis on a reversed-phase C-18 column in THF–H_2O gave a number of components. The first peak (20%) corresponded to the reduced Pc and a second peak (30%) was characterized as hetero-dimer **5a**: HRMS MALDI-TOF: *m/z*, 2500.06; UV–vis (DMF) λ_{max} 677 nm and 710 nm. On similar treatment of monoiodo tri(1′-indolylsulfonyl)ZnPc (**4b**)[4c] and 1,2,3,4,8,9,10,11, 15,16,17,18-dodecafluoro ZnPc[12] (**4c)** with **2**, hetero-dimer **5b** (15%) (MS: *m/z*, 1858.8; λ_{max} 671, 692 nm) and **5c** (20%) (HRMS, MALDI-TOF: *m/z*, 1538.2; λ_{max} 641, 680 nm) were obtained along with the corresponding reduced Pc.

This Pc-synthon reaction was also used for the synthesis of a Pc–$(Pc)_2$ branched triad. The Pc-boronate complex **2** and 2,3-diiodo-9,16,23-tri-*tert*-butyl ZnPc[13] (**6**) (1:2.2 molar ratio) were dissolved in toluene under nitrogen, catalyst Pd_2dba_3, S-Phos, and K_3PO_4 were added and the mixture was heated at 90 °C for 3 h. From the reaction mixture, two main products were separated by reversed-phase C-18 chromatography in THF–H_2O. The first product was characterized as a homo-coupled dimer[9] (20%) and the second product as the trinuclear Pc-based triad **7** (20%) (Fig. 3). The structure of this triad was established from MS MALDI-TOF: *m/z*, 2231-2238 (isotopic pattern); HRMS: calcd for $C_{132}H_{116}N_{24}Zn_3$: 2233.77; found 2233.3 (100.0%) and characteristic Q-band in the UV–vis spectrum. This triad is a first example of a symmetrically π-conjugated branched trinuclear Pc with units connected directly by C–C linkages. All Pc–Pc hetero dyads and triad are mixtures of regioisomers since they are derived from the isomeric monomers **2**.

The optical features of the hetero binuclear chromophoric system in methanol, THF, and DMF were compared to that of the corresponding parent monomers. The electronic absorption spectrum of the hetero-binuclear Pc **5a** in DMF showed a split Q-band, an intense maximum at 710 nm, and less intense band at 677 nm while Q-band maxima of monomer **2** were observed at 672 and 695 nm, respectively (Fig. 4). Soret-bands appear in the UV-region between 355 and 360 nm. The homo-coupled dimers show new red-shifted Q-bands due to the enlargement of the π-conjugated system and intramolecular electronic coupling between the two sub-units.



a: R= X=OCH_2CF_3: b: R=H; X= SO_2-Indole
c: R=X=F

Figure 2. Synthesis of Pc–Pc hetero-dimers.

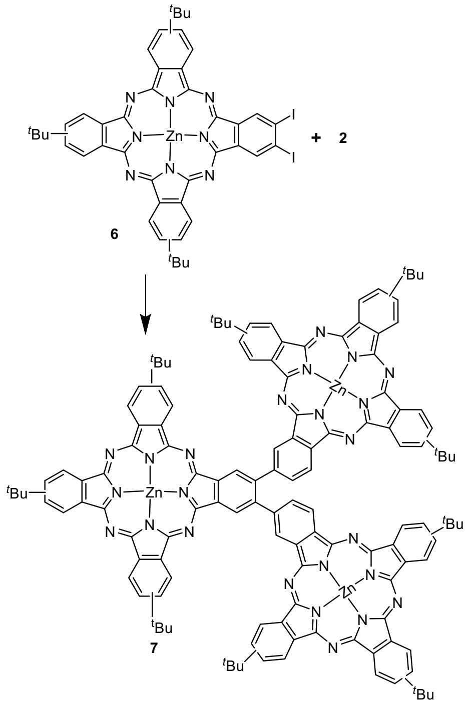


Figure 3. Synthesis of Pc–$(Pc)_2$ homo-triad.

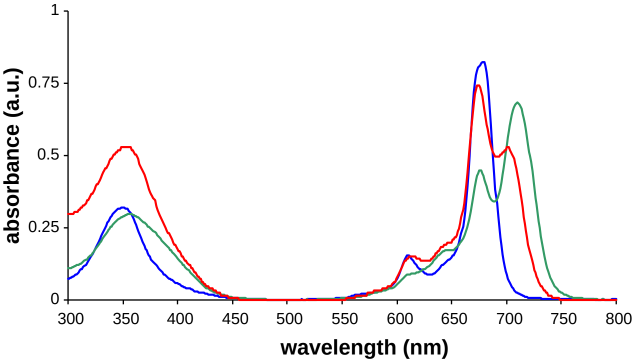


Figure 4. Electronic spectra (DMF) of 4-borane(t-bu)$_3$ZnPc **2** (blue), the hetero-dimer **5a** (red), and triad **7** (green).

The less prominent bathochromic shift of the split Q-band observed with **5a** are likely due to differences in the planarity of the two homo-coupled products.

The electronic absorption spectrum of the homo-trinuclear Pc **7** also shows split Q-bands, that is, a major peak at 704 nm and a less intense band at 676 nm. The intensity of the latter and extent of the bathochromic shift are less prominent as compared to that observed with the homo-dimer,[9] probably due to extensive steric hindrance resulting in non-planarity, reduced dihedral angles and less conjugated π-system (Fig. 4).

In summary, we report the synthesis of a Pc-boronate synthon using Pd-catalyst coupling with arylhalides and its application for the preparation of novel covalently C–C linked Pc–Pc hetero-dimers and Pc–(Pc)$_2$ homo-triad. Photophysical data reveal π-conjugation between the sub-units in accordance with the overall planarity of the molecules.

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