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Synthesis of phthalocyanine dimers, trimers, and oligomers bridged via phenyl groups

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ABSTRACT

Several phthalocyanine dimers, trimers, and oligomers bridged via aryl (phenyl) groups were prepared using the Suzuki–Miyaura cross coupling reaction of phthalocyanine-boronate ester and various halide derivatives under palladium catalyst reaction conditions. Photophysical data reveal energy transfer between the Pc moieties resulting in the appearance of new red-shifted Q-bands. The shift and the nature of Q-band depend on the number of phenyl groups, the number of Pc, and the position of attachment on the phenyl ring.

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Phthalocyanines (Pc) were discovered by chance and readily found applications as blue and green dyestuffs and pigments.¹ Pc possess outstanding chemical and electronic properties, including strong absorption in the visible region, rendering them of interest for diverse fields of applications. Pc and structurally related tetrapyrrolic macrocycles have been studied for applications in catalysis, biomimetic model systems for primary processes of natural photosynthesis, dyads for use in optic-electric devices, chemical sensors, electrochromism, super molecular assemblies, active components in semiconductors, information storage systems, and liquid crystal displays.² They have been also extensively studied as photodynamic agents for medical applications including the treatment of cancer, age related macular degeneration (AMD), and germicides, as well as diagnostic cancer imaging agents.³

Transition metal catalysts have found many successful applications in organic syntheses. Among them, Pd-catalyzed coupling reactions have evolved as versatile, powerful tools for the formation of C–C bonds in the synthesis of Pc and porphyrins.⁴ The reported Pd-catalyzed coupling reactions of Pc using halogenated Pc templates provide an interesting route to synthesize new families of unusually elaborated Pc macrocycles.

A variety of Pc dimers and oligomers have been prepared, including homo- and heterodimers and oligomers of Pc, tetraazaporphyrins (TAPs), naphthalocyanines (Ncs), subphthalocyanines (SubPcs),⁵ and pyrazinoporphyrazines (PyZs).⁶ These compounds have interesting properties and they found applications in

numerous important technological fields. For the synthesis of conjugated and non-conjugated Pc dyad systems, different rigid or flexible spacer groups have been used to connect the two chromophores. Planar homo-dimers of Pc sharing benzene or naphthalene rings have also been reported.⁷ Pd-catalyzed coupling reactions using Pc-halide monomers for the synthesis of directly, covalently linked Pc–Pc homo-dimers (*ortho* and *meta*) connected via a C–C bond of the Pc-benzene rings, have been described.⁸ We have previously prepared the Suzuki Pc-boronate synthon and reported its successful application for the single-step, Pd-catalyzed synthesis of Pc–Pc homo and hetero dyads, Pc–Pc triads, Pc–Por dyads, and Pc–Por–Pc triads, directly linked via a C–C bond.⁹

We now report the synthesis of a series of binuclear, trinuclear, oligomers, and cofacial ZnPc derivatives. In the direct linked molecules, the two and three Pc rings are attached directly at different positions of the Pc-phenyl ring while in the cofacial systems the two Pc rings are linked via the 1,8-positions of naphthalene and benzoquinone. Suzuki type cross coupling reactions using Pc-boronate synthon **1** are exemplified. Initially the coupling reaction of **1** with 1,4-diiodobenzene using Pd₂dba₃ or Pd(0) resulted either in the formation of the reduced analog of Pc **1** or a coupling product, along with the dehalogenated product **2**. Alternatively we used a benzene ring in which two halo groups of different reactivities were attached. Pc **1** was coupled with 1-bromo-4-iodobenzene (in which the iodo is more reactive than the bromo) in DMF under argon at 90 °C, using PdCl₂(dppf) as catalyst and K₂CO₃ as base. The reaction proceeded smoothly and after 2 h product **3** was isolated in 70–80% yield along with a small amount of reduced

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Pc. To compare the effect of attachment at *meta*- and *ortho*- versus *para*-coupling on the photophysical properties, we prepared the corresponding homo-coupled dimers. Thus the coupling reaction of Pc **1** with 1-bromo-3-iodo and 1-bromo-2-iodo benzene was performed using the above reaction condition to give **4** and **5** respectively. In all cases the coupling product was formed as a major product, along with the reduced Pc (Scheme 1).

HRMS analysis of the coupling products gave the expected molecular ion m/z 901.24 and characteristic UV–Vis (THF) absorption peaks at λ_{max} 674, 608, 347 nm together with a strong Q-band. Two ZnPc complexes bridged through a phenyl ring were prepared using the above coupling products **3–5**. Thus the bromophenyl-Pc derivatives **3–5** were treated with Pc-synthon **1** in DMF under argon at 90 °C using PdCl₂(dppf) as catalyst and K₂CO₃. Purification on silica gel using 5% EtOAc in toluene, followed by analytical HPLC on a C-18 reversed phase column using a linear gradient of THF–H₂O, gave coupling products **7–9** in 20–30% yield along with the reduced Pc. All Pc–Ph–Pc are mixtures of regioisomers since they are derived from isomeric monomers. HRMS analysis of all coupling products (**7–9**) gave the expected molecular ion m/z 1566.6. The optical features of these chromophoric systems in THF differ from those of the corresponding parent monomer (Fig. 1). Monomer **3** shows a sharp Q-band at 674 nm, while the spectrum of dimer **7**, in which the Pc are attached at the 1,4 positions (*p*) of the phenyl ring, shows two Q-bands at 689 and 675 nm of about similar intensities (Fig. 1). The peak at 675 nm is at the same position as the absorption maximum of the monomer, while the second, bathochromic-shifted peak at 689 nm corresponds to the dimer. A similar spectral pattern was observed for Pc **8**, with Pc attachments at the 1,3 positions (*m*) of the phenyl ring. The electronic absorption spectrum of the dimer Pc **9**, with Pc substituents at the 1,2 phenyl (*o*) positions, likewise showed two Q-bands at 685 and 670 nm. However the bathochromic shift of the split Q-band showed a lower intensity as compared to that observed with the *p*- and *m*-analogs. These splitting patterns most likely reflect on the planarity of the coupling products. The relatively planar geometry conformation allows for conjugation between

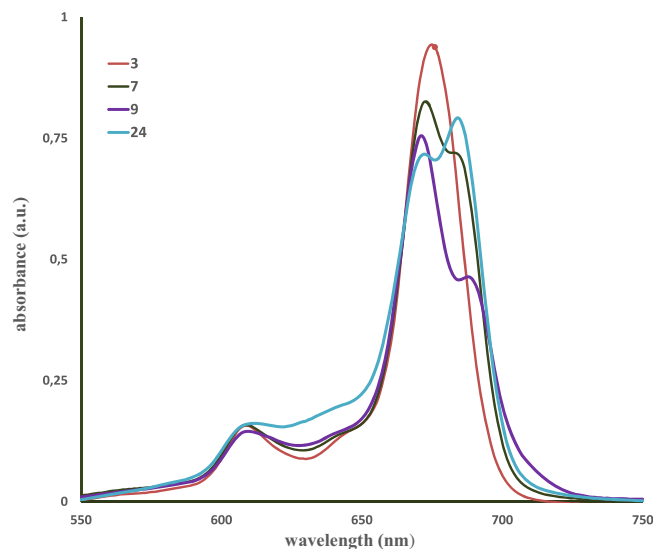
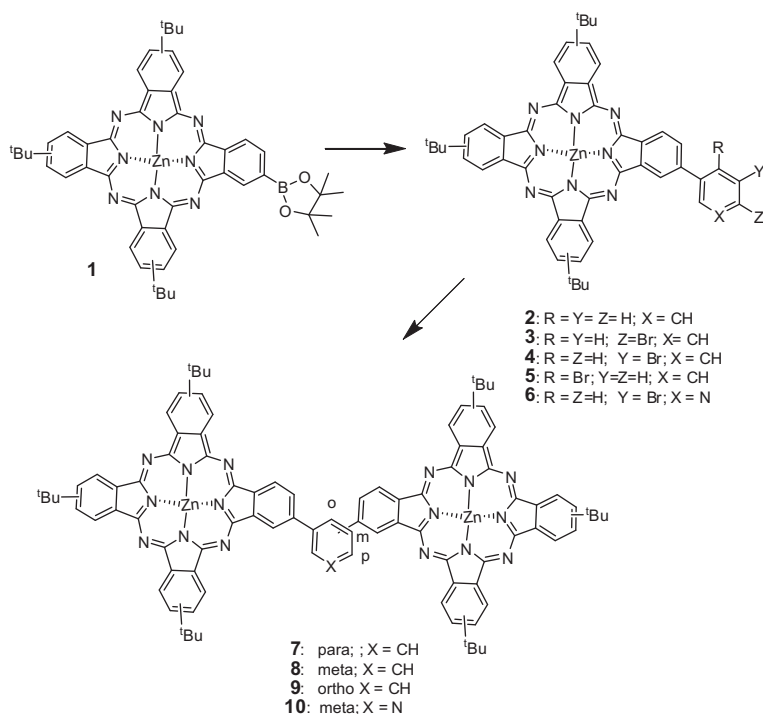


Figure 1. Electronic spectra of Pc derivatives (THF) of **3** (red), **7** (green), **9** (purple), and **24** (blue).

the two Pc molecules through the phenyl coupling unit. In the *ortho*-substituted dimer the planar conformation is not allowed due to steric hindrance. Consequently the degree of conjugation is lower as compared to that observed with the *para*-isomers. This phenomenon was far less pronounced as observed for similar complexes where the two Pc units are coupled directly via a benzene moiety.⁸

The binuclear Pc **10** bridged via a pyridine unit was also prepared in two steps. First Pc **1** was reacted with 3,5-dibromopyridine to give compound **6** followed by coupling with Pc **1**.

In order to prepare oligo Pc, the boronate **1** was reacted with 4,4-dibromobiphenyl in the presence of catalyst PdCl₂(dppf) in DMF under argon at 90 °C to yield mono adduct **11**. Reductive



Scheme 1. Phthalocyanine dimers bridged via a phenyl group.

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