# Hexa-peri-hexabenzocoronene-porphyrinoids as models for functional graphenes in the development of newer materials.

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# ABSTRACT

Cyclocondensation of 5-(hexaphenylbenzene)dipyrromethane with 3,5-(di-*tert*-butyl)benzaldehyde in presence of acid followed by oxidation with DDQ gave 5,15-bis(hexaphenylbenzene)-10,20-(3,5-di-*tert*-butyl phenyl)porphyrin which on cyclodehydrogenation with ferric chloride in dichloromethane gave 5,15bis(hexabenzocoronene)-10,20-(3,5-di-*tert*-butylphenyl) porphyrin as model for functional graphene-porphyrin.

*Keywords*: Hexabenzocoronene, porphyrinoids, graphene, newer materials, molecular electronics.

### INTRODUCTION

Graphene, an important allotropic member of carbon, has received much attention owing to its exceptional thermal and electrical and electrical conductivity, interesting properties in material science with wide range of applications in energy devices, electronics, catalysis, sensors and biomedicines.<sup>[1,2]</sup> Pristine graphene is a zero band gap semimetal material and nanoribbon graphene with width smaller than 10nm is semiconducting material suitable for electronic devices.<sup>[3]</sup> Bottom up organic synthesis have been used to synthesize the nanographenes with well defined structures.<sup>[4,5]</sup> The opening of gap in graphene have been realized by defect formation, chemical dopants, electrical and magnetic fields and interaction with various gases.<sup>[6]</sup> The noncovalent interaction of large polycyclic aromatic hydrocarbons with graphene is an important method of opening of large band gaps.<sup>[7]</sup>

The large polyaromatic hydrocarbons are well defined cutouts of graphene and they are called nanographenes.<sup>[8]</sup> The graphene nanoribbon,<sup>[9]</sup> a narrow strip of nanographenehas attracted much attention due to its unique optical, electrical and spin properties. The covalent modification of graphene with porphyrinoids have been used to modulate the chemical and physical properties of pristine graphene and to alter the band gap of graphene for development of newer materials for electronic and other applications.<sup>[10]</sup>

Polycyclic aromatic hydrocarbons are important building blocks for the construction of organic semiconducting materials <sup>[11a,b]</sup> and model compounds for asphaltene fractions of bitumen and heavy oils.<sup>[11c]</sup> Functional hexa-peri-hexa benzocoronenes (HBCs) and

related poly aromatic hydrocarbons (PAHs) are regarded and studied as models for graphene. The chemical modifications of HBC periphery with long alkyl chains form the discotic liquid crystalline materials,<sup>[12a,b]</sup> whereas modification with amphiphilic side chains lead to graphitic nanotubes arrays.<sup>[12c]</sup> Chromophores and various other subsitituents to HBC molecules lead to various sensor materials and organic solar cells. The inclusion of substituents change the properties of new HBC materials but the electronic properties of the HBC core remain the same.<sup>[13]</sup> The synthesis of 5,10-diarylporphyrins have been synthesized bv cyclo condensation of 5-aryl dipyrromethanes with aromatic aldehydes catalysed by sulfonated graphene as solid acids and examined the noncovalent interaction with pristine graphene by us recently.<sup>[14]</sup> Now we report the synthesis of covalently linked polycyclic aromatic hydrocarbons with porphyrins, characterization and their electronic properties in different reaction conditions.

#### **RESULTS AND DISCUSSION**

oxidative cyclodehydrogenation The route from hexaphenylbenzene to hexa-peri-hexabenzocoronene is an important method for the synthesis of HBC materials.<sup>[15]</sup> The synthesis of the targeted conjugate hexabenzocoronene-porphyrin was initiated to proceed via precursor hexaphenylbenzene-aldehyde (HPB-CHO). The condensation of a statistical mixture of aldehyde HPB-CHO, 4-*tert*-butylbenzaldehyde and pyrrole in dry dichloromethane was performed at room temperature under argon atmosphere for 3 hr followed by the oxidation with DDQ gave crude residue which was purified by column chromatography on silica (chloroform : petroleum ether, 1:2) to obtain mono-hexaphenylbenzene porphyrin (HPB-POR 1a) in 14% yield by following literature procedure.<sup>[16]</sup> The compound (1a) was characterized by UV-visible, <sup>1</sup>H NMR AND MS data.

This mono hexaphenylbenzene-porphyrin (1a) further undergoes subsequent oxidative flattening via Scholl oxidation reaction of the hexaphenylbenzene ring by using ferric chloride as oxidant. A solution of ferric chloride in nitromethane was added to solution of hexaphenylbenzeneporphyrin (1a) in ice-cooled dichloromethane under argon atmosphere. The resultant dark brown solution was quenched by pouring the solution into methanol and the



resultant crude product was purified by column chromatography to give the porphyrin (2a) in 78% yield.(Scheme 1) We could not record the <sup>1</sup>H NMR in CDCl<sub>3</sub> When we introduce 3,5-di-tert-butyl group in benzaldehyde to prepare corresponding porphyrins (1b and 2b), they are soluble in CDCl<sub>3</sub> which show similar chemical shifts as reported in literature.<sup>[17]</sup>



Figure 1: a) UV-Vis spectrum of HBC, mono HPB-POR and mono HBC-POR in o-dichlorobenzene; b) Emission spectrum of HBC, mono HPB-POR and mono HBC-POR at excitation wavelength,  $\lambda = 420$  nm.

In the UV-Visible spectrum of (2), the most intense pband transition of hexabenzocoronene was observed at 353 nm. A hypsochromic shift was seen from 353 nm (reference hexa-<sup>t</sup>butyl-hexabenzocoronene) to 347 nm for the conjugate which was attributed to the formation of aggregates and supramolecular self-assembly in solution. The Soret band of the porphyrin (2) shows a bathochromic shift from 419 nm in precursor (1) to 425 nm in (2) and reduction in the extinction coefficient of the soret band and the four Q-band had been observed. These spectral changes indicate electronic interaction between the HBC and porphyrin unit in porphyrin (2).

In fluorescence spectrum of (2) on excitation at 420 nm complete quenching of the corresponding HBC emission was observed and emission occurred only from the porphyrin unit at 658 nm and 725 nm. similar result was also observed on the excitation of (2) at 350 nm whereas in the absence of covalent coupling, i.e. no interaction between both HBC and porphyrin was observed.



5-(hexaphenylbenzene) of The cyclocondensation dipyrromethane with 3,5-di-tert-butylbenzaldehyde in presence of acid followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDO), gave 5.15bis(hexaphenylbenzene)-10,20-(3,5-di-tert-butyl

phenyl)porphyrin (3) in 6 % yield. The peripheral  $\beta$ ,  $\beta'$ protons appear downfield whereas NH protons appear upfields (-3.00 ppm) in the <sup>1</sup>H-NMR of porphyrin (3). The Soret band appears at 421 nm and other four O-bands at 521, 567, 605 and 649 nm in the UV-Visible spectra of 1in chloroform solution. Further, the molecular ion peak at m/z

has appeared at 1752.82 which confirmed the formation of porphyrin (3). The cyclodehydrogenation of porphyrin (3) with FeCl<sub>3</sub> in dichloromethane gave 5,15-bis(hexabenzocoronene)-10,20-(3,5-di-*tert*-

butylphenyl)porphyrin (4) in 78 % yield. The structure of above porphyrin was confirmed by characteristic UV-Visible, NMR and other spectroscopic data. The appearance of peak at 356 nm, Soret band at 430 nm and four Q-bands at 521, 567, 605, 649 nm with reduced intensity in the UV-Visible spectrum of porphyrin (4) indicate the aromatization and electronic interaction in porphyrin (4).

The cyclocondensation of 5-(3,5-di-tert-butyl-4-hydroxyphenyl) dipyrromethane with 1-(4-formylbenzene) pentaphenylbenzene (HPB-CHO) in the presence of acid followed by oxidation with DDQ gave 5,15-bis(hexaphenylbenzene)-10,20-(3,5-di-tert-butyl-4-hydroxy phenyl)porphyrin (5) in 6 % yield. The appearance of a sharp singlet at -2.80 ppm in higher field and higher field and eight  $\beta$ -pyrrolic proton in lower field and peak for hydroxyl at 5.37 nm indicate the formation of porphyrin (3). Further the appearance of molecular ion peak at m/z at 1782.86 confirms the formation of porphyrin (5). The oxidation with ferric chloride and DDQ did not gave the corresponding hexabenzocoronene linked porphyrin.



The interaction of hydroxyl porphyrin (5) with tetrabutylammonium fluoride shows a bathochromic shift in

UV-Visible spectral studies and a red shift along with almost quenched spectrum in emission studies indicates the formation of a new quinone type intermediate along with a drastic color change from purple to green. (Scheme 3)<sup>[18]</sup> Introduction of functional groups after the synthesis of HBC core is generally difficult due to low solubility<sup>[19]</sup> and the presence of reactive substituents often induces undesired reaction during the oxidation of hexaphenylbenzene precursors with FeCl<sub>3</sub>.<sup>[20]</sup>

#### Conclusions

Various covalent hexabenzocoronene-porphyrin hybrids have been synthesized by oxidative cyclodehydrogenation method as model for graphene-porphyrins. The UV-Visible and emission spectroscopic studies indicate the electronic interaction between porphyrin and hexabenzocoronene. The presence of hydroxy group on porphyrin moiety also prevents the oxidative cyclodehydrogenation of hexaphenylbenzene porphyrin to hexabenzocoronene porphyrin.

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