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Hyper Branched Helicenes: Synthesis, Characterization and its Application towards CO_2 Sorption

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Abstract. A novel hyper branched helicenes (HBHs) derived from α, α'-dichloro- *o*-xylene monomer through simple Friedel Crafts alkylation route using ferric chloride as the catalyst and 1, 2-dichloroethane as the solvent. The resulting materials was brown in color and its shows the maximum absorbance towards longer wavelength region from 200 to 1000 nm. The HBHs structural elucidation was confirmed by FTIR spectroscopy. The morphology of the samples was unveiled by SEM and TEM techniques. The porous nature of the prepared materials was determined by N_2 sorption isotherms. They are amorphous and showed CO_2 absorption between 5 and 6 weight t% sorption at room temperature. They are hydrophobic. They decompose above 300 °C in air. So, in addition to its application to sorption of CO_2, they are also materials of right choice for the fabrication of supercapacitors and organic solar cells.

Keywords: α, α'-dichloro- *o*-xylene; adsorption; hyper branched polymers; Friedel Crafts reaction; supercapacitors

1 Introduction

We are all well-known, carbon dioxide (CO_2) is one of the primary anthropogenic greenhouse gas (GHG) as well as the leading culprit in global warming, inadequate environment and vulnerable climate change. Carbon capture and storage (CCS) technology that efficiently capture CO_2 from existing emission sources is seen as one of the most promising solutions to slow down climate changes [1]. Among many carbon capturing technologies, capturing CO_2 by porous materials is an excellent and advanced approach due to its energetic efficiency and economical competitiveness [2]. Various porous adsorbents existing at present to capture CO_2, such as activated carbons [3], zeolites [4], hydrotalcite [5], amine-functioned porous materials [6, 7], metal–organic frameworks (MOFs) [8] and hypercross-linked polymers [9-14].

Helicenes are polycyclic aromatic compounds with non-planar screw shaped skeletons formed by ortho-fused benzene or other aromatic rings [15, 16]. The first

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helicenes was developed by Meisenheimer and Witte in 1903 [17]. They are largely used in the fields of non-linear optics and circularly polarized luminescence. They also serve as discotic liquid crystals and conjugated polymers. Their rigid helical framework, high optical stability and unique chiral array with functional groups such as -OH, -NH_2, -CN etc., have made them useful as chiral catalysts in asymmetric synthesis. They are commonly prepared by photocyclizing of stilbene, and methods without light are also employed. There are ample literatures available for CO_2 sorption [18-21].

We have developed a very simple method of obtaining helicenes by Friedel Crafts reaction of α, α'-dichloro- *o*-xylene in the presence of Ferric Chloride. The same reaction was also carried out with naphthalene and anthracene. They are highly branched too. Their synthesis, characterization and applications are discussed.

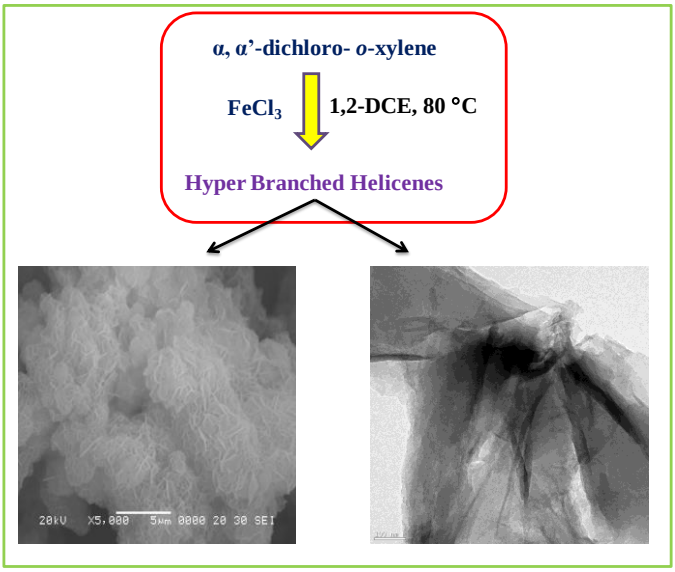

Fig. 1. Schematic representation of the synthesis of Helicenes and their microscopy images

2 Experimental

2.1 Materials

α, α'-dichloro- *o*-xylene was purchased from Sigma Aldrich (USA). Ferric chloride was purchased from Kanto Chemicals Co., Inc. Tokyo. Other chemicals like acetone, concentrated HCl, 1, 2-dichloroethane and methanol were purchased from Daejung Chemicals, South Korea.

2.2 Synthesis of hyper branched helicenes

3.5 g of ferric chloride and 20 mL of 1, 2-dichloroethane was taken in a 100 mL RB flask provided with the magnetic pellet. The flask was placed in a heating mantle. 2.0 g of α, α'-dichloro-*o*-xylene dissolved in 30 mL of 1, 2-dichloroethane was slowly added to it and the mixture stirred well. After 20min of stirring the temperature of the mixture was raised to 40 °C. After 4 h the temperature was raised to 80 °C and the reaction continued for 20 h. The flask was cooled to room temperature and the contents were filtered under suction. The residue was washed with methanol, 5% HCl in acetone water mixture (1:1), water and finally with acetone, and dried in the oven at 100 °C for 12 h. The final product named as HBH-1 (Hyper branched helicene). The procedure was repeated with naphthalene and anthracene and named as HBH-2 and HBH-3 respectively.

Table 1. Reaction protocol of hyper branched helicene synthesis

S. No.	α, α'-dichloro o-xylene (g)	Ferric chloride (g)	1,2 dichloroethane (mL)	Temperature (°C)
HBH	2.0	3.5	30	80

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