

Abstract

The contents of the present thesis entitled *“Synthesis of Polycyclic Aromatic Hydrocarbons with Extended π -Conjugation via Multi-Fold C-C Coupling Reaction and Their Versatile Applications”* have been divided into four chapters based on the results achieved from the experimental work carried out during the entire course of the PhD research program.

Chapter I provides a brief literature survey on synthesis of π -conjugated polycyclic aromatic hydrocarbons (PAHs) through C-C cross-coupling reactions. The versatile application on photophysical properties, sensing, optoelectronic device and cytotoxic potential is also discussed. The chapter ends with a discussion on the scope of the current thesis.

Chapter II formulates a single step multi-fold Sonogashira reaction to access nine new symmetrical tetraalkynylatedanthracene employing $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2/\text{cataCXium}^{\text{®}}\text{A}$ with moderate to good yields. Five of these tetraalkynylated anthracenes have been characterized by single crystal X-ray crystallography, with two of them exhibiting numerous interactions that significantly shorten the inter-planar distances in the solid-state structure. Solvatochromism and halochromism are exhibited by these tetraalkynylated anthracenes with one of them showing a low band-gap of 1.79 eV. The rich photophysical properties exhibited by these molecules in solution and in the solid-state offer immense promise for future applications in sensors and optoelectronic devices.

Chapter III investigates the multi-fold Sonogashira coupling reaction of aryl halides with aryl acetylene in the presence of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.5 mol%) as catalysts, $\text{CataCXium}^{\text{®}}\text{A}$ (1 mol%) as monodentate phosphine ligand, an equivalent of Cs_2CO_3 under copper-free and amine-free conditions in a readily available green solvent at room temperature. The protocol is applicable for single as well as multi-fold Sonogashira coupling reaction to access various polycyclic aromatic hydrocarbons. Six of these have been tested for their anticancer properties on human triple-negative breast cancer (TNBC) cell line MDA-MB-231 and human dermal fibroblasts (HDF). The compounds being intrinsically fluorescent, their cellular localization was checked by live cell fluorescence imaging. The death of the cancer cells was triggered by polyalkynylatedanthracene molecules through necrosis and apoptosis.

Chapter IV discusses about the development of a new efficient synthetic protocol for single and multi-fold Suzuki coupling reaction in a single step with moderate to excellent yields employing the highly earth abundant, readily available and inexpensive nickel salts with good functional group tolerance. $\text{ArI} > \text{ArBr} > \text{ArCl}$ is the reactivity order of the halides towards the reaction which follows the corresponding C-X (X=I, Br, and Cl) bond strength. EPR analysis, mercury-drop experiments and reactions with radical scavenger such as TEMPO point to the involvement of well-defined molecular species that operate via a Ni(0)/Ni(II) catalytic cycle where oxidative addition of the aryl halide to Ni(0) is likely to be the rate-determining-step (RDS). For the first time, valuable new polycyclic aromatic hydrocarbons (PAHs) with exciting photophysical properties have been synthesized via Ni(II) catalyzed multi-fold Suzuki coupling.

The current thesis demonstrates a new efficient synthetic protocol for polyarylated/alkynylatedanthracenes via multi-fold C-C cross coupling reactions. They exhibit tunable photophysical properties and are semiconducting in nature. These compounds have been studied for various applications such as sensors and are potential cytotoxic agents.