

CHAPTER I

INTRODUCTION

The expectations of decreasing fossil fuel usage and increasing environmental concern have encouraged the research on inexpensive renewable energy source. Solar energy is the largest energy source available on the earth. Harvesting energy directly from sunlight using photovoltaic (PV) cells is broadly recognized as a promising approach to future global energy production. Nowadays, inorganic solar cell is dominating the present market, while organic solar cell has been developed for recent years. Compared with inorganic solar cells, organic solar cells have several advantages to increase energy conversion efficiency by various methods [1-3]. Therefore, the interest for research on organic are radically increasing because of low-cost cell fabrication, ease of modification of photoactive compound, and possibility for making flexible devices.

Organic solar cells based on heterojunction blending of electron donating and accepting materials in which nanoscale phase separation is created to achieve both quantitative charge generations after photo-excitation and effective collection of these charge. While the bulk-heterojunction solar cells are greatly developed, dye-sensitized solar cell is one of the most popular organic solar cells. Its primary structure consists of a metal electrode, photoactive compound binding on TiO₂ surface and electrolyte. Among all organic photosensitizer, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) dyes, often referred to as “semi-porphyrins”[4], are among the most recent investigated fluorescent dyes for a variety of analytical and imaging applications [5, 6] due to their favorable photophysical and optoelectronic properties that include high photostability, high extinction coefficients, and high fluorescence quantum yields. Moreover, BODIPYs have attracted special interest in drug discovery [7], biomedical imaging [8], and optical sensing [9, 10]. BODIPY is generally composed of a dipyrromethene π -system and a boron difluoride core. Modification of the BODIPY structure has been developed in order to tune the absorption and emission wavelengths, increased solubility and enhanced charge transfer ability. Introduction of substituents at pyrrole *meso*-position and boron moieties has afforded a variety of BODIPYs, electronic structures of which are greatly influenced not only by the π -system modification at the dipyrromethene moiety but by the substitution of core fluorine atoms [11].

Over the past decade, interest in the BODIPY dyes fused with external aromatic rings at the β -carbon atoms has considerably increased [12]. Often referred to as “ π -extended BODIPYs”, these dye systems possess many interesting properties, inviting applications in many branches of material research and biomedical technology [13]. Due to their high planarity, extended π -conjugation and rigidified molecular framework, the spectral features of this class of annotated BODIPY dyes are much sharper and well-defined, with their absorption and emission wavelengths shifted considerably farthest to the infrared [14].

Among the rigid ring extended BODIPY systems, molecules such as dibenzo-fused BODIPYs (hereafter abbreviated as benzo-BODIPYs) have become one of the most widely used building blocks for the construction of pH sensors [12] molecular switches and light-emitting polymers [15], biolabeling reagents, and photovoltaic cells [16]. Benzo-BODIPY dyes often possess high rigidity in their structure which leads to a high fluorescence quantum yield in solution as well as strong intermolecular π - π interactions in the solid state, the factors beneficial for their applications as π -functional materials [17]. In structural terms, these ring expanded and annelated BODIPY dyes are closely related to the tetrabenzoporphyrins (TBPs) and can be conveniently referred to as “half-TBPs” (Chart 1-1).

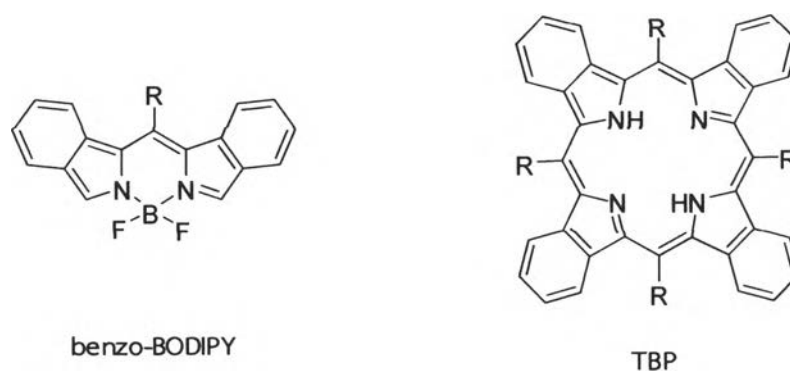


Chart 1-1: The general structures of benzo-BODIPY and TBP

Thiophene derivatives have been found to exhibit a wide range of biological activities and active compounds as chemotherapeutics [18], while many have also been used in various materials science applications [19-21]. Moreover, oligo- and polythiophenes are among the best investigated and most often used as π -

conjugated materials, in particular as a photoactive compound in organic optoelectronic devices and molecular electronics [22].

In this research, we synthesized BODIPY compounds bearing thiophenyl unit at the *meso*-positions and benzo-BODIPYs, starting from thermodynamically stable 4,5,6,7-tetrahydroisoindole ester. While we were hopeful that these new systems would exhibit red-shifted spectral features, the principle motivation for this work was to investigate the effect of the structural modification on the BODIPY core including benzannulation of pyrroles and the thiophenyl *meso*-substitution on the photophysical and electrochemical properties of the BODIPYs in order to obtain practical approaches for designing suitable extended conjugation systems for the optoelectronic applications.

1.1 Objectives of this research

The objectives of this research are to synthesize benzo-BODIPYs (1-4) (Chart 1-2) and to investigate their photophysical and electrochemical properties for the potential use in optoelectronic devices.

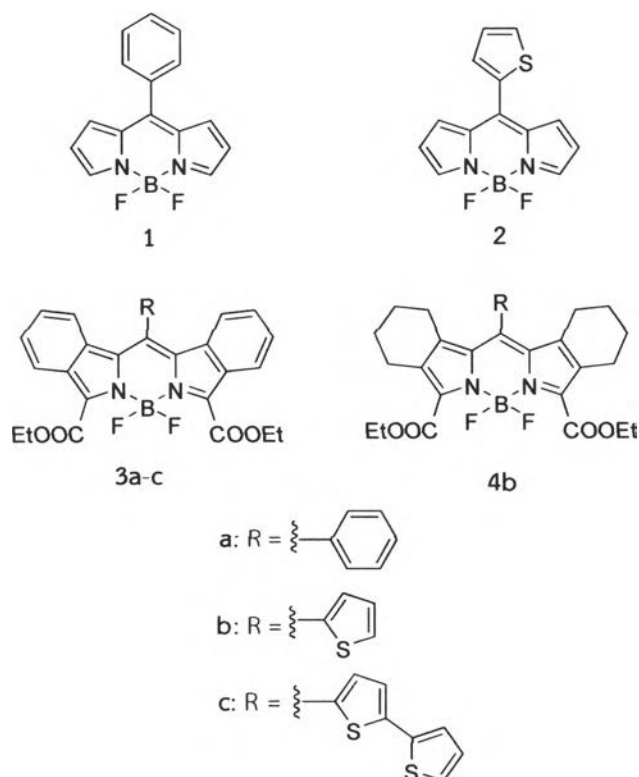


Chart 1-2: Target BODIPYs

1.2 Scope of this research

The scope of this research covers the synthesis of benzo-BODIPY compounds bearing mono- and bithienyl unit at the meso positions. All new compounds were fully characterized by various spectroscopic techniques *i.e.* mass spectrometry, and $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. Photophysical properties were investigated by UV-Vis and fluorescence spectrophotometry.

