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Aza-BODIPY: As an Organic Photovoltaic Material

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Abstract

A short overview of the applicability of aza-BODIPY dye and its derivatives in organic photovoltaics are provided. Properties and working technique of organic photovoltaic cell is briefly discussed followed by Synthesis, structure and light absorption properties of aza-dipyrromethenes and its BF2 chelated aza- BODIPY.

Key Words: Aza- BODIPY, PV technology, semiconductors, Fluorescence

Introduction

Globally increasing demand of energy raised the human efforts to produce energy which is one of the major causes of increase in global warming.1,2 Photovoltaic technologies potentially tenders solution to this challenge. Photovoltaic (PV) technology offers numerous benefits over conventional energy sources. The biggest benefit of this technology is the capability to produce clean and unsustainable source of energy without costing pollution. Photovoltaic (PV) technology offers transformation of solar energy into electricity. It is one of the most capable opportunity in the field of renewable energy. One can define photovoltaic device as a device having the capacity to transform light into electricity.3 Modern photovoltaic devices tend to incorporate pn junctions in semiconductor layers, where photovoltaic potential is developed.4 Organic semiconductors are the compounds which has light absorption properties as well as ability to conduct charges through the molecular structure. They can be p-type or n-type. Conjugated polymers such as PPV5-8, MEH-PPV9-14, MDMO-PPV15-19, P3HT20-24, P3OT25-29, PEDOT-PSS30,31 and PCPDTBT32-38 have been used as p-type organic semiconductors.32-38 There are several small molecules which has also been used as PV material, the most common moieties are phthalocyanine (Pc)39-45, pentacene46-50, merocyanine(MC)51,52 etc. There have been few studies on the use of derivatives of dipyrromethene (BODIPY)53-57 and fewer still on aza-dipyrromethene (Aza-BODIPY)58-59. The factors which affecting the performance of solar cells are absorption coefficient, hole mobility, diffusion length, exciton, thin film morphology and band gap. For the ideal donor, there are some evident desirable characteristics like higher light absorption tendency as well as possessing high extinction coefficients.60 These small molecules acts as donors in the active layer part of OPV cells.

There are various advantages of small molecules over the use of large polymers in OPV device:

- Structural rigidity of small molecules offers easy purification as well as abolish the problems associated with macromolecules like discrepancy in molecular weight, polydispersity index and structural regioregularity.
- Small molecules have high absorption coefficients which permit the use of active layer of lesser thickness and thus enhance charge transfer.
Structural tune up and determination of its effect on the efficiency of OPV devices are much easier than those of large polymer molecules.

Fig 1: The polymers commonly used in OPV cells

Fig 2: Small molecules commonly used in OPV cells
Organic Photovoltaic cell:
An Organic photovoltaic (OPV) cell or organic solar cell is a category of solar cell which uses organic polymers or small organic moieties for absorption of light and charge separation to generate electricity from solar energy. An organic solar cell generally consists of a p-type and an n-type of semiconductor which act as donor and acceptor respectively, joining area between these donor and acceptor is the heterojunction. Absorption of light results excitons, which disperse to this p-n heterojunction interface and separate into free holes and electrons and are transferred into the electrodes. Provided the remarkable performances of OPV devices, the projection of having economical OPV cells in the near future are good.

Properties and Operation of Organic Photovoltaic Devices:
Organic photovoltaics works on the same mechanism as the photosynthesis process works in plants. During photosynthesis chlorophyll pigment absorbs sunlight which induces charge separation, and further produces oxygen and organic compounds by conversion of carbon dioxide, water and minerals. Operation of an organic solar cell consists of three steps: light absorption, charge separation and charge transport. The active layer of an organic solar cell comprises of two types of substance a donor and an acceptor, donor absorbs light and generates the exciton which further results in charge separation i.e. separation to electron and hole or return back to the ground state. When this charge separation attains electrode before merging with each other, produces polarons which generate current. Since this charge separation is strictly limited to the boundary of donor and acceptor, therefore for efficient working of PV devices chemical structural of active layer is of utmost importance.

Generation of photocurrent is an essential function of a solar cell, and current generation is determined by a balance between light absorption, charge carrier generation and recombination. The initial electronic exciton process leads to production of charge carriers, while recombination an electronic relaxation process reduces the number of free charge carrier. Upon absorption of a photon, charge carrier generation occurs as a result of the promotion of an electron from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital), subsequent electron transfer from donor to acceptor and charge separation.

![Diagram of organic cell operation](image-url)
BF₂-Aza-dipyrrromethenes (Aza-BODIPYs):

Pyrrrole is one of the most important heterocyclic aromatic compound and a building block for a variety of organic molecules and polymers. BF₂ chelated dipyrromethene, and BF₂ chelated azadipyrrromethene dyes have been one of the interesting and exclusively investigated types of pyrrole compounds. Since past ten years, based on their long-wavelength absorptions and intense emissions of aza-BODIPYs various studies have been carried out on the applicabilities of these complexes in several fields.

Difluoro-bora-1,3,5,7-tetraphenyl aza-dipyrrromethe is the simplest form of aza-BODIPY derivatives. The aza-BODIPY centre comprises of two pyrrole rings linked through a nitrogen atom.

![Fig 4: structures of (1) BODIPY indicating IUPAC numbering (2) Difluoro-bora-1,3,5,7-tetraphenyl dipyrromethene boron difluoride (3) aza-BODIPY (4) 1,3,5,7-tetraphenyl aza-dipyrrromethene boron difluoride.](image)

Dipyrrromethenes (DIPYs) were first synthesized in 1930s, but study of their spectral properties and metal complexes were carried out later. For the first time synthesis of boron difluoride chelated dipyrromethene (BODIPY) complex was investigated in 1966. Complexation of BF₂ by reacting dipyrromethene with boron difluoride etherate (BF₃.OEt₂) gave BF₂- BODIPY centre.

The unique spectral properties like intense absorption in UV region with sharp fluorescence and high quantum yield shown by BF₂- BODIPY attracted interest of several investigators. Due to the presence of fully conjugated framework of the BODIPY, makes it convenient for its structural modification to enhance the spectral and fluorescence properties. The aza-BODIPY is obtained by the substitution of the meso-carbon atom bridging (position 8) with a nitrogen atom. The first synthesis of aza-dipyrromethene (aza-DIPY) was reported in 1946, but BF₂ chelated aza-dipyrromethene (aza-BODIPY) was first synthesized by Boyer et. al in 1993. Due to its lengthy preparation, the aza-BODIPYs have been studied less in contrast to BODIPY.

**Synthesis of Aza-BODIPYs:**

O'Shea et al proposed synthesis of symmetrically substituted aza-BODIPYs and also optimized the reaction conditions by incorporating new solvent and using ammonium acetate as different ammonium source replacing ammonium formate. Synthetic route of aza-BODIPY involves four steps. In the very first step chalcone (1,3-diphenyl-2-propen-1-one) is prepared by aldol condensation of acetophenone and benzaldehyde. Second step involves conversion of chalcone into its nitro derivative (1,3-diphenyl-4-nitrobutane-1-one) by Michael addition reaction with nitromethane using diethylamine as base. Precursor compound 1, 3-diphenyl-4-nitrobutane-1-one undergoes chemical transformation in the presence of ammonium source to produce aza-dipyrromethene in third step.
The fourth and final step involves chelation of BF$_2$ molecule to aza-dipyromethe by simply reacting it with boron trifluoride etherate (BF$_3$.OEt$_2$).

Scheme 1: Synthesis of aza-BODIPY. (i) KOH, EtOH, room temp, 24 h. (ii) CH$_3$NO$_2$, diethylamine, MeOH, Reflux, 24 h. (iii) NH$_4$CO$_2$H, EtOH, reflux, 24 h. (iv) BF$_3$.OEt$_2$, N,N-diisopropylethylamine, CH$_2$Cl$_2$, room temp, 24 h.

Another route for synthesis of symmetric BF$_2$ chelated aza-dipyromethenes (aza-BODIPY) (Scheme 2) only differ from the previous one merely in the synthesis of aza-DIPY. Here, precursor 1,3-diphenyl-4-nitrobutane-1-one converted into the pyrrole derivative via chemical transformations which further undergoes condensation reaction with another pyrrole molecule to give aza-DIPY. BF$_2$- BODIPY synthesized by reacting aza-DIPYs with boron trifluoride etherate at room temperature.

Scheme 2: The formation of symmetrical aza-BODIPYs
Synthesis of asymmetric aza-BODIPY incorporates conversion of 2, 4-diarylpyrroles into its 5-nitroso derivatives by Michael addition of nitro methane followed by condensation with another pyrrole molecule.\(^{68}\)

**Scheme 3:** The general synthetic route of unsymmetrical aza-BODIPY

One of the other methods of preparation of the derivatives of intermediate compound aza-dipyrromethenes (aza-DIPY) is the reaction of Grignard reagents such as phenyl magnesium bromide with succinonitrile or thalodinitrile molecules.\(^{69,70}\)

**Scheme 4:** synthesis of aza-dipyrromethenes (aza-DIPY) using Grignard reagents

Another method for synthesis of symmetric and asymmetric conformationally restricted aza-BODIPYs comprises condensation of cyclicized and restricted pyrrole with nitrosopyrrole and further coplexation with boron trifluoride.\(^{71}\)
Scheme 5: Synthesis of conformationally restricted aza-BODIPY. Reagents and conditions: (i) 1) HOAc, Ac₂O, NaNO₂ 2) Hunig’s base BF₃.OEt₂(CH₂Cl)₂. (ii) 1) HOAc, NaNO₂ 2) aryl pyrrole, Ac₂O, HOAc 3) Hunig’s base BF₃.OEt₂(CH₂Cl)₂

Spectral Properties of aza-BODIPYs:

O’Shea et al.⁶⁶ have investigated that the UV absorption maxima of BF₂-chelated tetraaryl-aza-dipyrromethenes largely depends on the nature of substituents as well as position of the aryl groups. Red shift in absorption maxima along with increase in the extinction coefficients observed with electron-donating groups on 5-aryl substituents while fewer effect monitored on absorption maxima with electron-donating groups at the 3-aryl position.

![Scheme 5: Synthesis of conformationally restricted aza-BODIPY](image)

**Fig 5:** Spectroscopic properties of some of the aza-BODIPYs with different groups

Chelation of Aza-BODIPY derivatives with mercuric ion leads to characteristic red shift in UV- VIS absorption region elevate interest for chemosensors.⁷²

![Chelation of Aza-BODIPY derivatives with mercuric ion](image)

**Fig 6:** spectroscopic properties of aza-BODIPY chelated with ion.
Comparing spectral properties of conformationally restricted aza-BODIPYs with the normal aza-BODIPYs it has been observed that there is approximately 50 nm shift in absorption. Incorporation of carbocyclic rings either on one or both sides of aza-BODIPY showed significant chemical and photo stability with strong fluorescence emission.

Applicability of Aza-BODIPYs in Organic solar cells:
Depending on the intense absorption of Aza-BODIPYs IR region and easy modification of their spectroscopic properties by introduction of different substituents on positions 1, 3, 5 and 7 of the dipyrrin core, these compounds have been explored widespread for use in organic solar cells. Mueller et al in 2012 reported the use of aza-BODIPYs in solar cells and established the utility of aza-BODIPYs as donor materials with PC60BM as an acceptor. Compound 4 shows power conversion efficiency of 1.2% with enhanced Voc (0.96V). A device using compound (5) offer a power conversion with an efficiency of 1.1% showing Voc of 0.65 V. This decrease in cell voltage than the former can be explained on the basis of compound (5) have small energy gap. By using compound (7) a strong power conversion efficiency of 2.63% has been attained. The major aspect which influences efficiency of the solar cell is the energy gap between HOMO and LUMO of the donor and acceptors respectively. On comparing energy level aspects of Compounds (4) and (7) with compounds (5) and (6) it has been observed that the former have the lower energy offsets than later compounds. All the research work done in this direction has shown immense possibility of usability of aza-BODIPY molecules and its derivatives in organic photovoltaic cells.
It has been observed that introduction of electron donor substituents viz. thiophene to the aza-BODIPY shift the absorption maxima into the red spectral region. Introduction of electron donating group increases energy of HOMO, while the energy level of LUMO remains constant, and this results in decrease of the band gap. Evidently the energy levels of HOMO and LUMO of compounds (8), (9) and (10) increases considerably. Among them, compound (10) showed the major alteration in the HOMO energy level compared to compound (4), consequently, compound (11) might have the best donor capacity.

Conclusions:
In this short review we are mainly focused on the spectroscopic properties of aza-BODIPY and further its applicability in photovoltaic technique. Light absorption properties of these compounds have raised interest of researchers in last decade. We have attempted to cover all the work done yet in the direction of exploring light absorption properties as well as synthetic routes of aza-BODIPYs and its application in PV technology.
References: