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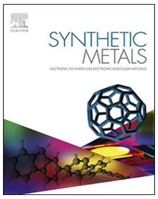

Small biomolecule dopant retinals: Electron blocking layer in P3HT:PCBM type organic solar cells

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ABSTRACT

We present a comparative study of the photophysics and electron/hole properties of all-*trans* retinal-benzimidazole type molecules decorated with different electronic moieties (such as $–OCH_3$, $–N(CH_3)_2$, –F, $–CF_3$) in organic photovoltaic (OPV) devices in solution and on solid thin films. Steady-state spectra of synthesized dyes give large Stokes shifts (6887–13152 cm^{-1}) in studied solvents. Decay times of these dyes were found to be substituent dependent giving a bi-exponential decay for fluorine containing retinals. *Trans* to *cis* photoisomerization rate constants of synthesized dyes were found to be about 3.3–16.4 × $10^{-6}\,s^{-1}$. Using a cyclic voltammetry measurements, HOMO and LUMO energy levels of fluorine-substituted dyes shift to lower values as compared to that of unfluorinated derivatives. We compared unusual electron blocking behavior of methoxy- and *N,N*-dimethylamino-substituted derivatives (**Ret-I** and **Ret-II**, respectively) in bulk heterojunction solar cells (BHJ-SCs) incorporating an active layer of P3HT:PCBM doped with Ret derivatives at various weight ratios. Hole mobility values for fluorine containing retinals were found to be about 1.0×10^{-4} and $7.1 \times 10^{-4}\,cm^2/V\,s$ for **Ret-III** and **Ret-IV** dyes, respectively.

1. Introduction

Retinal (Vitamin A aldehyde), a chromophoric polyene that can be easily produced by an organism, is used for initializing process in vision events by interacting with the light. It can be obtained by irreversible oxidative cleavage reaction from carotenes [1] in the presence of β-carotene 15,15′-monooxygenase [2] or β-carotene 15,15′-dioxygenase enzymes [3]. *trans*-retinal structure can be transformed into an 11-*cis* configuration through a series of photochemical reactions and forms the natural vision pigment [4]. In the presence of molecular oxygen, when retinal is excited by UV or blue light, inter-system crossing occurs effectively into its triplet state at which energy transfer is easily occurred into molecular oxygen to produce singlet oxygen and other reactive oxygen species [5,6].

Retinal gives specifically Schiff base formation reactions known in the literature, because of electrophilic reactivity of aldehyde group in its structure [7–9]. Its fluorous derivatives have also been synthesized in order to use in the interaction mechanism of retinal with polar structures. They exhibit high electronegativity and low bulk property caused by the nature of fluorine atoms [10]. It has been reported that C-13 substituent variation of the incorporated retinal group in bacteriorhodopsin has given a bathochromic shift of about 60–65 nm when a methyl group is replaced by CF_3 substituent at C-13 position of the structure [11]. In another study, new types of retinal chromophores were synthesized by monofluorination from different positions of the structure, and their Schiff base derivatives were prepared and incubated with bacteriorhodopsin. Effect of the electrostatic attractions between fluorine groups and protein structure was investigated by means of optical absorption changes [12].

There has been no information about efficient use of retinal groups in solar cell systems such as OPV, bulk heterojunction solar cell (BHJ-SC) or optoelectronic devices such as organic field-effect organic transistor (OFET), and organic light emitting organic diode (OLED) technologies. In this study, we present new retinal-benzimidazole conjugates possessing different electronic subunits to investigate their unusual electron and hole transporting activities in OPV devices. We have experimentally monitored the UV–vis and fluorescence emission characteristics of synthesized retinal derivatives in different solvent of polarities. We have detected fluorescence lifetimes using single photon counting method to analyze their excited state behavior. Their photoisomerization kinetics in chlorobenzene solution under metal halide global (MHG) lamp irradiation were defined. We have fabricated photovoltaic devices in conventional, also ternary structures by adding Ret derivatives with different blending ratios in a configuration of ITO/

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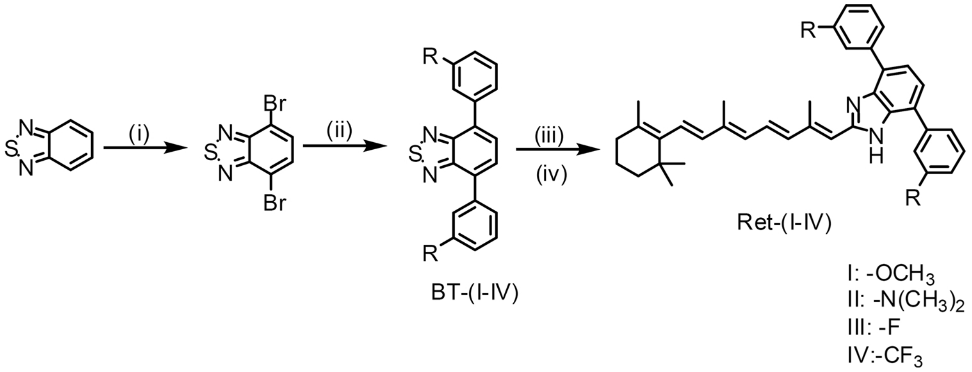

Scheme 1. Synthesis of **Ret-(I-IV)** dyes.
(i) Br_2/HBr, 120 °C [21]; (ii) Boronic acid derivative, 2 M Na_2CO_3, $Pd(PPh_3)_4$, EtOH/benzene, 85 °C [22]; (iii) $NaBH_4/CoCl_2$&903;$6H_2O$, EtOH/THF, 80 °C (for **Ret-I** and **Ret-II**) [23]; Zn/CH_3COOH, 50 °C (for **Ret-III** and **Ret-IV**); (iv) *trans*-retinal, MeCN, $Zn(OAc)_2$ [24].

PEDOT:PSS/P3HT:**Ret-(I-IV)**:PCBM/Al(100 nm).

2. Experimental section

2.1. General characterization techniques

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer, and using TMS as the internal reference. Infrared spectra were recorded on a Perkin Elmer-Spectrum BX spectrophotometer preparing KBr pellets. UV–vis absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer. The LC–MS/MS spectral analyses were performed using on an Agilent Technologies 1560 Infinity liquid chromatography system with a 6420 Triple Quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source. All samples were dissolved in Me-CN solution. The electrospray source of the MS was operated only in positive mode.

The optimized ground state geometry of **Ret-(I-IV)** dyes was used to calculate the molecular orbital energies in density functional theory (DFT) [13] calculations performed using the Gaussian 09W. Electronic excitations were computed B3LYP/6-31G(d) level [14]. Cyclic voltammetry studies of **Ret-(I-IV)** dyes were carried out on a CH instruments 660B-Electrochemical Workstation with platinum electrodes as counter electrodes at a scan rate of 100 mV/s against an Ag/Ag$^+$ reference electrode with a nitrogen-saturated electrolyte solution of 100 mM [TBA][PF6] in Me-CN. Potentials were referenced to the ferrocenium/ferrocene redox couple by using ferrocene as an internal standard and its oxidation potential was detected at +0.57 V. Onset values of E_{red}, E_{ox}, and other parameters were calculated according to the equation [15]:

$$E_{HOMO} = -e(E_{ox}^{onset} + 4.8);\ E_{LUMO} = -e(E_{red}^{onset} + 4.8)$$
$$E_g^{opt} = {}^{1240}\!/_{\lambda_{abs}^{onset}};\ E_{HOMO} = E_{LUMO} - E_g^{opt}$$

The fluorescence decay times and time-resolved fluorescence spectra of **Ret-(I-IV)** dyes in the four solvents have been determined by the single photon counting method (FLS 920 Edinburgh) at the excitation wavelength of 368.8 nm. The fluorescence decays were analyzed globally using the Edinburgh Instruments F900 exponential tail fit method [16]. The quality of the fits has been judged by the fitting parameters such as $\chi^2 \leq 1.2$ [17]. All measurements were performed in 1 cm optical path length cuvettes. Atomic force microscopy (AFM) images were obtained in non-contact mode using an Ambious Technology Q-Scope 250 Model instrument to observe the surface morphology of thin films.

2.2. Materials

[6,6]-Phenyl C_{61}-butyric acid methyl ester (PCBM), poly(3-hexylthiophene-2,5-diyl) (P3HT), 3-(*N,N*-dimethylamino)phenylboronic acid, 3-methoxybenzeneboronic acid, 3-fluorophenylboronic acid, 3-(trifluoromethyl)phenylboronic acid, tetrakis(triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$), and all *trans*-retinal were purchased from Sigma Aldrich. Sodium carbonate (from Carlo Erba) and $CoCl_2{\cdot}6H_2O$ (from Alfa Aesar) were used as received. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. 4,7-Dibromo-2,1,3-benzothiadiazole, **BT-I**, and **BT-II** were synthesized according to reference [18]. Scheme 1 represents the synthesis of **Ret-(I-IV)** dyes and their precursors.

2.3. OPV device fabrication, photovoltaic and mobility measurements and testing

Effect of synthesized **Ret-(I-IV)** dyes in conventional configuration ITO/PEDOT:PSS/**Ret-(I-IV)**:PCBM/Al(100 nm), ITO/PEDOT:PSS/P3HT:**Ret-(III-IV)**/Al(100 nm) and ternary structures with different weight ratios are investigated. Solutions of photoactive components in 1,2-dichlorobenzene were mixed at concentrations of 2 wt% in different mass ratios and stirred overnight. Indium tin oxide (ITO) deposited glass substrates from Delta Tech. Corp. (2.5 × 2.5 cm in size) with R_{sheet}: 10 Ω/sq conductivity were sequentially cleaned by deionized water, sonication in acetone, and isopropanol for 15 min each, respectively; and dried with nitrogen. Then, the glasses were cured with oxygen plasma generator under 10^{-2} mbar pressure for 5 min. PEDOT:PSS (AL4083) in water was spin-coated on the pre-cleaned ITO substrates with 4000 rpm for 30 s, then annealed at 120 °C for 30 min. The pre-formed solutions of P3HT, PCBM, and **Ret-(I-IV)** dyes were spin-coated (1000 rpm), and dried at 120 °C for 30 min in a N_2 filled atmosphere. The Al (100 nm) metal electrode was thermally deposited on the top of the BHJ-SC active layer. Spin coating processes of the electron blocking layer and active layer were performed in an air and, then device was completed by electrode evaporation in thermal evaporator equipped MBRAUN 200 B glove box. All characterizations were done under inert atmosphere in glove box.

Devices for space-charge-limited current (SCLC) measurements were fabricated in a manner similar to the solar cell devices with the structures of ITO/PEDOT:PSS/**Ret-(III-IV)**/Au(30 nm). I–V characteristics were measured by a computerized Keithley 2400 source meter in the dark and under simulated AM1.5G illumination at 100 mW/cm^2 supplied by a MHG lamb (375 W). The mobilities were determined by fitting the dark current using an equation given below:

$$J_{SCLC} = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{L^3}$$

where ε_o is the permittivity of free space, ε_r is the dielectric constant of the Ret film, μ_h is the hole mobility, V is the applied voltage and L is the thickness of the photo-active layer [19,20].

2.4. Synthesis

2.4.1. General procedure for suzuki coupling reactions (Procedure A)

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (1 mol equiv.) and aqueous 2 M sodium carbonate solution (15 mL) in benzene (35 mL)