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Bromo-substituted cibalackrot backbone, a versatile donor or acceptor main core for organic optoelectronic devices

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ABSTRACT

Cibalackrot (**Ci-I**), one of the latest highly conjugated compound possessing *bis*-lactam structure, was investigated with respect to their brominated derivatives in order to determine their suitable substitution points for the syntheses of new class of small molecules for optoelectronic devices. 7,14-*Bis*(4-bromophenyl) (**Ci-II**) and 3,10-dibromo (**Ci-III**) derivatives of cibalackrot possess moderately narrow band gaps of 2.15 and 2.09 eV, respectively. Notably, **Ci-III** dye exhibits more red-shifted ultraviolet–visible (UV–vis) absorption and fluorescence emission spectra as compared to that of **Ci-II** dye because **Ci-III** shows more prominent intramolecular charge transfer (ICT) complex than that of **Ci-II** dye. Electron mobilities of the order of 7.0×10^{-4} cm^2/V and 3.1×10^{-4} cm^2/V were measured using **Ci-II** and **Ci-III** as active layer, respectively. Charge transfer properties of the molecules were investigated in bulk heterojunction device configuration wherein **Ci-III** showed p-type behavior against n-type PCBM in photovoltaic device. Photovoltaic performance of **Ci-III** dye which was used as donor component is 20 times higher than that of the device in which this dye was used as acceptor.

1. Introduction

Nowadays, there are increasing efforts on structural variations of conjugated polymers and small molecules for optoelectronic devices in order to obtain the most suitable structural design for managing high performance devices. Such kind of variations tailored by electron donor (D) and electron-acceptor (A) groups of the main core have great impact on optoelectronic parameters such as optical bandgaps, fluorescence characteristics, absorption profiles, and ionization potentials [1]. Organic photovoltaics (OPVs) have gained a considerable attention in the area of solar light-energy conversion systems owing to their low cost, flexibility and remarkable lightweight [2]. A considerable tendency of the molecular design for OPVs are externalized on attachment of different D or A subunits to the suitable position of the electroactive backbone. These provide a wide range of molecular arrangements of functional molecules for OPVs.

Among the several small organic molecules with electroactive core, cibalackrot dye [3,4], a bay-annulated indigo derivative, has received considerable attention for its excellent ambipolar charge transport property [5,6], high conjugated structure, excellent electron acceptor property [7], high fluorescence quantum yield [8], low-lying LUMO energy level, and narrow optical band gap [9]. Cibalackrot dye gives long-wavelength absorption profile with its maximum absorptions around 540–560 nm [8] due to the enhanced π-electron resonance localized between the indole and lactam segments of the structure. Typically, it is noted that strongly-bound localized excitons in the highly-disordered organic semiconductors are the result of low dielectric constant. Higher dielectric constants can be observed in molecules with the higher degree of order such as cibalackrot dyes ($\varepsilon = 4.8$) as compared to indigo dyes ($\varepsilon = 4.3$) [7]. Proton transfer pathway through intramolecular hydrogen bond is blocked because of highly-annulated structure of cibalackrot as compared to that of indigo/tyrian purple type dyes, which exhibit an efficient excited state deactivation pathway due to the proton-exchange mechanism [7,8].

Noting that annulation pathway through cibalackrot ring opens up new category of design for acceptor type molecules. In cibalackrot platform, oxindole units of indigo are fixed into a coplanar geometry where carbonyl groups and nitrogen atoms are annulated through acetyl chloride group to form *bis*-lactam structure of cibalackrot [6,10].

Despite these advantages of cibalackrot dyes over other organic

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molecular acceptors, there are limited number of their applications in OPV devices. To the best of our knowledge, only few attempts have been made to investigate OPV devices using cibalackrot dye as the photo-active layer. Bronstein et al. reported charge transport and photodiode properties of a cibalackrot polymer in organic electronic devices. This polymer exhibits high ambipolar transport in OFET device of 0.23 cm^2/V, and also OPV device efficiencies up to 2.35% [11]. Liu et al. explored the electrochromic efficiency of a cibalakrot polymer giving high optical contrast in the visible and near-infrared region, good coloration efficiency and long term stability [12].

In this work, cibalackrot core was brominated to its phenyl or indole rings (Scheme 1) in order to investigate the relationship between substitution points of the structure and photovoltaic performance. Their absorption-emission profiles and fluorescence decay kinetics were investigated in different solvents of polarities. Their electrochemical properties were evaluated in electron mobility measurements and photovoltaic performances.

2. Experimental

2.1. Materials and reagents

The main reagents used for the synthesis of cibalackrot dyes, 4-Bromo-2-nitrobenzaldehyde and phenylacetyl chloride were purchased from Sigma Aldrich and Merck Company, respectively. *Tetrakis*(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) catalyst was purchased from TCI company. All other chemicals and solvents were purchased from Merck, and used without further purification. Photovoltaic materials [6,6]-Phenyl C_{61}-butyric acid methyl ester (PCBM) and poly(3-hexylthiophene-2,5-diyl) (P3HT) were purchased from Sigma Aldrich.

2.2. Analytical instruments

^1H and ^{13}C NMR spectra were obtained using a Bruker 400 MHz spectrometer. Chemical shifts were reported as ppm relative to the TMS standard (0 ppm). FT-IR spectra were monitored on a Perkin Elmer-Spectrum BX spectrophotometer with samples prepared as KBr pellets. The optical properties of the dyes were investigated by both UV–Vis spectroscopy using a Perkin Elmer Lambda 950 spectrophotometer and fluorescence emission spectroscopy using a FLS 920 Edinburg instrument in different solvent of polarities in 1 cm optical path length cuvettes. Single photon counting results and fluorescence decays were analyzed globally using the Edinburgh Instruments F900 exponential tail fit method [13] at the excitation wavelength of 472.4 nm. The quality of the fits has been judged by the fitting parameters such as $\chi^2 \leq 1.2$ [14]. All spectroscopic measurements in solution were done at optical density around 0.1.

2.3. Electrochemical measurements and DFT calculations

The electrochemical properties of the dyes were performed in an acetonitrile solution with 0.1 M tetrabutylammoniumhexafluorophosphate $[TBA][PF_6]$ as the supporting electrolyte, glassy carbon as the working electrode, a Pt wire as the counter electrode, and a Ag/Ag^+ as the reference electrode using a CH instrument (660B-Electrochemical Workstation) at a scan rate of 100 $mV\,s^{-1}$. Potentials were referenced to the ferrocenium/ferrocene redox couple by using ferrocene as an internal standard and its oxidation potential was detected at +0.63 V. Onset values of E_{red}, E_{ox}, and other parameters were calculated according to the equation [15]:

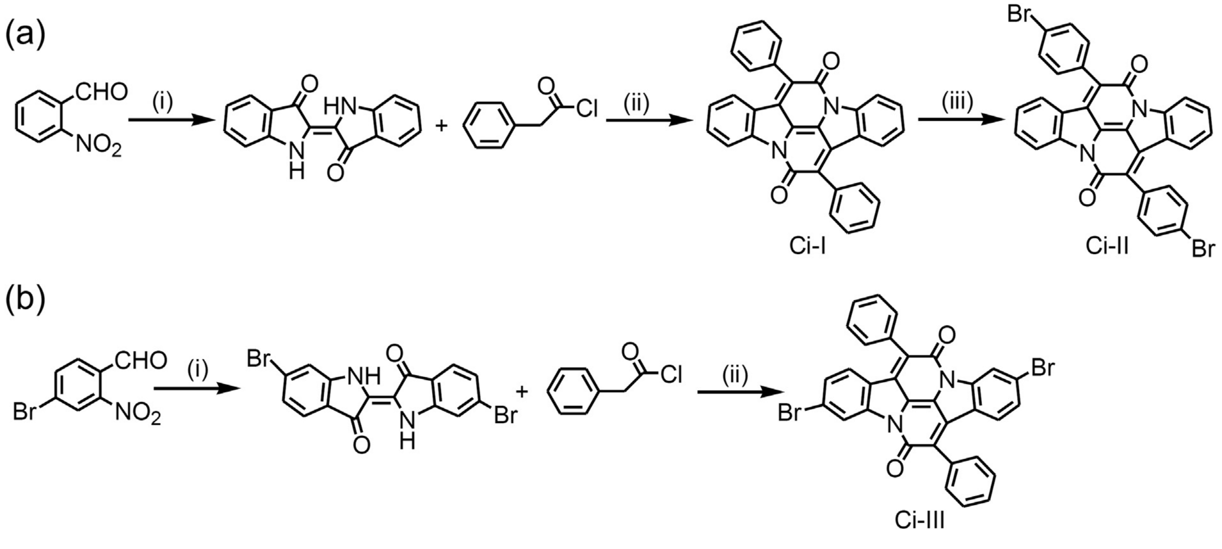
$$E_{HOMO} = -e\left(E_{ox}^{onset} + 4.8\right); E_{LUMO} = -e\left(E_{red}^{onset} + 4.8\right)$$

$$E_g^{opt} = {}^{1240}\!\big/_{\lambda_{abs}^{onset}};\ E_{HOMO} = E_{LUMO} - E_g^{opt}$$

The electronic structures of **Ci-II** and **Ci-III** molecules were investigated using DFT and TD-SCF [16] with B3LYP/6-31G(d) basis [17], as implemented in the Gaussian 09 package. The UV–vis absorption spectra of **Ci-II** and **Ci-III** dyes were also calculated by TD-SCF. Oscillator strength (f) calculated by time dependent density functional theory were presented as 0.7063, and 0.5475 for **Ci-II** and **Ci-III**, respectively.

2.4. Fabrication and characterization of OPV devices

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 cleaned using a deionized water, acetone, and isopropanol for 10 min each by sonication, and dried under a stream of nitrogen.



Scheme 1. Synthesis of (a) **Ci-II** and (b) **Ci-III** dyes. **(i)** Acetone:water (1:1), NaOH, ice bath, then room temperature [4]; **(ii)** xylene, 140 °C, 48 h, reflux [8]; **(iii)** N-bromosuccinimide, $CHCl_3$, room temperature [6].