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Extended isoindigos as building blocks for developing D–A-type conjugated polymers†

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By using 5-bromo-*N*-tetradecylindolin-2-one and different dialdehydes in a double Knoevenagel condensation procedure, three new π -extended isoindigo-based monomers (**3**, **5** and **7**) were synthesized. π -Extended isoindigo-based monomers were coupled with 2,2-bithiophene to create donor–acceptor conjugated polymers **P-1**, **P-2** and **P-3** by using a Stille coupling procedure. The polymers were characterized by ¹H NMR, thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). Photophysical and electrochemical studies were carried out for the monomers and polymers. Polymers **P-1**, **P-2** and **P-3** show band gap values of 2.55 eV, 2.16 eV and 2.15 eV, respectively. The polymers have good thermal stability with a decomposition temperature (*T_d*) above 200 °C. The structural aspects of polymers **P-1**, **P-2** and **P-3** were studied by DFT calculations on model polymers (by replacing *N*-alkyl by *N*-ethyl groups) comprising the repeat unit of each parent copolymer, which indicates that the polymers are highly planar with the dihedral angle less than 30°. The powder X-ray diffraction (PXRD) analysis showed that polymer **P-3** exhibited greater crystallinity compared to polymer **P-1** and it surpasses polymer **P-2** in this aspect. The measured space-charge-limited current (SCLC) hole mobilities were found to be $7.11 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $6.43 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $8.19 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for polymers **P-1**, **P-2** and **P-3**, respectively.

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Introduction

In recent years, a plethora of conjugated polymers have been explored as new-generation optoelectronic materials for organic electronic devices, such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaics (OPVs).^{1–4} Optoelectronic devices based on organic conjugated molecules and polymers possess many desirable characteristics, such as low-cost fabrication, flexibility, lightweight and ease of use over a wide surface area. Donor–acceptor (D–A) conjugated polymers have garnered significant interest in recent years as one of the most important classes of organic semiconductor materials, owing to their excellent performance in organic optoelectronic

devices and their ability to be tailored to specific structures to manipulate the semiconducting properties.^{5–9}

A large number of electron-donating building blocks for the D–A-type conjugated polymers have been studied extensively, such as 2,2'-bithiophene,¹⁰ thieno[3,2-*b*]thiophene,¹¹ 9-arylidene-9*H*-fluorene,¹² 9*H*-carbazole,¹³ 3,7-dialkyltetrathienoacene,¹⁴ 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene,¹⁵ *N*-alkyl dithieno[3,2-*b*:2',3'-*d'*]pyrrole,¹⁶ fused arylidipyrroles,¹⁷ benzo[1,2-*b*:4,5-*b'*]dithiophene,¹⁸ 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene,¹⁹ diinden[1,2-*b*:2',1'-*d'*]thiophene,²⁰ dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene,²¹ dithienocyclopentathieno[3,2-*b*]thiophene,²² and tetraalkylthieno[3',2':6,7][1]benzothieno[3,2-*b*]thieno[3,2-*g*][1]benzothiophene.²³ On the other hand, the progress in the development of electron-withdrawing building blocks lags behind compared to that of electron-donating building blocks. The most frequently used electron-withdrawing units include 2,1,3-benzothiadiazole,²⁴ *N*-heteroacenes,²⁵ alkyl carbonyl-substituted thieno[3,4-*b*]thiophene,²⁶ naphtho[1,2-*c*:5,6-*c'*]bis[1,2,5]thiadiazole,²⁷ thiazolo[5,4-*d*]thiazole,²⁸ and lactam- and imide-based acceptors. Imide-based acceptors such as naphthalene diimide,²⁹ perylene diimide,³⁰ and tetraazabenzodifluoranthene diimide,³¹ and lactam-based acceptors such as diketopyrrolopyrrole (DPP),³² indigo,³³ isoindigo,³⁴ benzodipyrrolidone,³⁵ dihydropyrroloindoleone,³⁶ indophenine,³⁷ thiophene-*S,S*-dioxidized

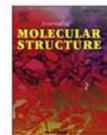
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Synthesis and study of indoloquinoline based D- π -A type conjugated molecules as fluorescent probe for hypochlorite detection

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ABSTRACT

We have successfully synthesized three new donor- π -acceptor (D- π -A) type indoloquinoline-based conjugated molecules in which electron rich indoloquinoline unit is coupled with different acceptor units such as barbituric acid, thiobarbituric acid and reduced isatin through thiophene spacer. All three molecules are characterized by IR, NMR and mass analysis. The photophysical, electrochemical, thermogravimetric analysis and DFT calculations studies were carried out for the synthesized molecules. The molecules were explored as a chemosensor for the detection of hypochlorite and the sensing mechanisms of these molecules towards hypochlorite were examined by ^1H NMR spectra. These molecules exhibit weak fluorescence emission due to a strong intramolecular charge transfer (ICT) effect between indoloquinoline moiety and different acceptors. Interestingly, compounds, **M1** and **M3** showed enhanced fluorescence recognition performance, whereas compound **M2** showed quenching fluorescence recognition performance for hypochlorite ion. Our study suggests that altering the D- π -A structure and employing suitable ICT effect can enhance the detection ability of molecules for the target analyte.

1. Introduction

Donor- π -acceptor (D- π -A) molecules are known for their good intramolecular charge transfer (ICT) capacity. The spectroscopic features of conjugated molecules with a D- π -A structure are linked to the donor to acceptor ICT excitations. Due to the ICT effects such D- π -A based conjugated molecules show significant importance [1,2] in optoelectronic technologies. D- π -A based conjugated molecules have been widely applied in fluorescence imaging, organic light-emitting diodes (OLEDs) [3–6], dye-sensitized solar cells (DSSCs) [7–9], sensors [10,11], transistors [12,13], and nonlinear optical technologies [14]. D- π -A based conjugated molecules having a push-pull type system are well known for their strong solvatochromism effects [15]. D- π -A based conjugated molecules are well-known as a fluorescent probe. The fluorescence properties of molecule can be enhanced by varying the D- π -A structures [16,17]. Fluorescent probes based on D- π -A molecules have high sensitivity, specificity, and high spatiotemporal resolution [18–20].

The electronic and optical characteristics of D- π -A molecules can be fine-tuned by structural modifications [21]. D- π -A molecule contains an electron donor fragment, such as; tetrahydroquinoline [22], triphenylamine [23], porphyrin [24], coumarin [25], indoline [26],

phenothiazine [27], carbazole [28], pyrene [29], etc., where as an acceptor fragment such as; malononitrile, cyanoacrylic acid, rhodanine-3-acetic acid, hydantoin, 2,4-thiazolidinedione, creatinine group, etc. [30]. Thiophene and its derivatives are well-known building blocks for D- π -A molecules. The polarizability of sulphur atom of thiophene stabilized the conjugated structure and provide a better charge-transport pathway [31,32].

6*H*-Indolo[2,3-*b*]quinoxaline (IQX) possesses unique features such as dipolar character, co-planarity, and ability to form π -stacked aggregates [33,34]. IQX are known for their application in OLEDs [27], DSSCs [21, 35] and as a hole-injection materials [16]. Donor-acceptor conjugated polymer based on IQX moiety exhibits high SCLC hole mobility. Moreover, strong π - π interactions and high planar framework were observed in single crystal X-ray diffraction studies of IQX-based molecules [36].

Numerous physiological processes in which reactive oxygen species (ROS) contribute significantly [37–39]. Hypochlorite ion (ClO^-) is an important ROS, which can provide essential immunity to human when attacked by microbes. In a biological point of view, ROS is the side product of the normal metabolism of oxygen. Hypochlorite ion is the product of a reaction between hydrogen peroxide and chloride ion in presence of myeloperoxidase catalyst in the phagosome of cells [40,41].

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Design and development of dithienopyrrolobenzothiadiazole-isoindigo based conjugated polymers and their hole mobilities

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Abstract

π -Extended dithienopyrrolobenzothiadiazole-isoindigo-based conjugated polymers were synthesized and well characterized by using various analysis techniques like infrared (IR), ¹H NMR, UV-Visible spectroscopy, thermogravimetric analysis, cyclic voltammetry analysis, and gel permeation chromatography. The bandgap of synthesized polymers, **P-1**, **P-2**, and **P-3**, were determined to be 1.95, 1.91, and 1.93 eV, respectively. These polymers exhibited robust thermal stability up to 290°C. The highest occupied molecular orbital energy levels were below -5.0 eV for all polymers, while the lowest unoccupied molecular orbital energy levels ranged from -3.5 to -3.3 eV. The measured space charge limited current hole mobilities for polymers, **P-1**, **P-2**, and **P-3**, were $1.02 \pm 0.47 \times 10^{-1}$, $1.17 \pm 0.47 \times 10^{-1}$, and $2.51 \pm 0.47 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

KEYWORDS

knoevenagel coupling reaction, dithienopyrrolobenzothiadiazole (DTPBT), isoindigo, donor-acceptor conjugated polymers

1 | INTRODUCTION

In recent decades, there has been extensive research and advancement in the field of conjugated polymers as highly promising electroactive materials. Conjugated

polymers have been thoroughly investigated for their application in affordable organic optoelectronic devices, including organic field-effect transistors (OFETs),¹⁻³ electrochromic devices,^{4,5} memory components,⁶ organic photovoltaic cells,⁷ and organic light-emitting diodes