



# Symmetrical and unsymmetrical donor–acceptor–donor organic dyes: Design, synthesis and characterization. Engineering panchromatic absorbance



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## ABSTRACT

A series of four novel organic semiconductor materials based on a donor–acceptor–donor (D–A–D) motif have been designed, synthesized and characterized to understand the effects of symmetry/asymmetry and acceptor strength. In this strategy, two symmetrical dyes with 2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde derived donor at both ends of the central acceptor and two unsymmetrical based on a 2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde derived donor on one end and an oligothiophene donor on the other end of the central acceptor were made. The central acceptors were dicyanovinylidene and 1,3-diethylthiobarbituric acid derivatives of 2-indanone in the set of symmetrical dyes and dicyanovinylidene in unsymmetrical dyes. The different acceptors allowed the tuning of optoelectronic properties. All the new materials were soluble in variety of organic solvents, such as chloroform, toluene and chlorobenzene. With the increasing acceptor strength, the wavelength of the longest wavelength absorption maximum as well as respective extinction coefficients were enhanced, which resulted in band gap reduction. The symmetrical molecules gave relatively narrow strong primary absorbances while asymmetric molecules gave weaker but double or very broad absorption peaks spanning the entire visible region to provide panchromatic absorption.

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## 1. Introduction

The design and development of intensely coloured organic dyes receives increasing attention for use in applications such as non-linear optics [1–3], two photon absorption and optical power limiting [4–7], optical data storage [8,9], 3D nanophotolithography [10], photo-refractive polymers [11–13] and organic photovoltaic devices [14]. Such dyes have a structure which allows the intramolecular charge transfer transition that broadens the absorption spectrum and reduces the optical band gap. The most commonly studied designs for such materials include, but are not limited to, donor–acceptor (D–A), D–A–D or A–D–A. In a typical design, an electron-donating fragment is connected to the electron-acceptor unit, either *via* conjugated double bonds or conjugated aromatic groups. Therefore it is not surprising that there is such growing

interest in the development of such designs by various D–A combinations with the goal of obtaining broader absorption over the whole visible region, appropriate energy levels and solution processability.

Intensely coloured conjugated polymers have received significant attention in field of bulk heterojunction photovoltaic devices [15–18]. While small molecule dyes are typically used for other applications, they have now relatively recently made significant inroads in the photovoltaic area [19–21]. The advantage of small-molecule dyes is in the ease of synthesis, introduction of structural variation, purification, less batch to batch variations and no end-group contamination. The required electronic properties of solution processable organic small molecules, depending on the application, are typically, low band gap, broad absorption profile, high extinction coefficients, multiple redox potentials and appropriate HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy levels. Panchromatic absorbance (300–800 nm) as well as the narrow band-gap can be achieved by engineering the chemical structure and incorporating appropriate donor/acceptor functionalities [19–21].

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In our efforts to design and develop novel materials for organic electronic applications [22–25], we have investigated D–A–D modular design and in this study, we report the design, synthesis and characterization of four new small organic molecules **R1**, **R2**, **R3** and **R4** as shown in Fig. 1 and the effect of symmetry and asymmetry on the design. All of these materials are based on the D–A–D architecture, where 2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde (MIA) derived donor has been chosen as a common donor at both ends of the central acceptor fragment so as to get symmetrical **R1** and **R2** dyes. In case of **R3** and **R4** dyes, MIA derived donor on one end and an oligothiophene was chosen for the other end of the central acceptor unit, thus generating a pair of asymmetrical D–A–D dyes.

The central acceptor group was derived from 2-indanone where it was modified by reacting with malononitrile to give 2-dicyanovinylideneindanone, which is an acceptor for **R1**, **R3** and **R4**. In dye **R2**, the central 2-indanone functionality was modified by reacting with 1,3-diethylthiobarbituric acid. When compared with the commonly used dicyanovinylidene group, the aromatizable 1,3-diethylthiobarbituric acid is an acceptor of greater strength when coupled with a lone electron pair donor such as an amine [3,24]. The combination of electron-donating units and aromatizable acceptors is a common strategy in non-linear dye design and provides large red shifts of lambda maxima over conventional acceptors like dicyanovinylidene [26]. An additional advantage of this aromatizable 1,3-diethylthiobarbituric acid acceptor unit is that a variety of alkyl groups can be located on the nitrogen atom to tune the solubility. In the present case, a simple ethyl group was the substituent of choice. These additional alkyl substitutions on the acceptor moieties not only enhance the solubility but also help for excellent film formation without crystallization. Similar substitutions could also be placed on the phenyl ring of MIA derived donor, however trimethyl groups provided adequate solubility for all of these molecules. Intramolecular charge transfer (ICT) would be enhanced with the use of an acceptor with increased acceptor strength, which in-turn would provide for greater light harvesting and perhaps better positioning of energy levels. Thus we should expect a bathochromic shift in absorbance for compound **R2** in comparison to **R1**. All the new materials, **R1**, **R2**, **R3** and **R4** were synthesized via the Knoevenagel condensation of appropriate aldehyde synthons with active methylene groups of the corresponding acceptor fragments and their chemical structures were confirmed by <sup>1</sup>H NMR spectroscopy and mass spectrometry. We were unable to synthesize **R3** and **R4** with aromatizable 1,3-diethylthiobarbituric acid acceptor fragment.

The molecules reported in this work were found to be highly soluble in a variety of conventional organic solvents such as dichloromethane, chloroform, chlorobenzene and toluene. High solubility is a desirable feature that is required for the fabrication of solution-processable organic semiconductor devices and precludes

the need for inclusion of electro-actively inert alkyl chains into the organic module. We systematically studied the effects of common and/or mixed donors and acceptors so as to achieve high extinction coefficients and/or panchromatic absorbance. To the best of our knowledge, this is the first examination of the effect of asymmetry on the D–A–D modular organic semiconducting materials.

## 2. Experimental details

### 2.1. Materials

All the reagents and chemicals used in various reactions, unless otherwise specified, were purchased from Sigma–Aldrich Co. Solvents used for various reactions were obtained from Merck speciality chemicals (Sydney, Australia) and were used as such. 2-(1*H*-inden-2(3*H*)-ylidene)malononitrile and 1,3-diethyl-5-(1*H*-inden-2(3*H*)-ylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione were synthesized as per the literature procedure [27].

### 2.2. Spectroscopic measurements

Unless otherwise specified, all <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker AV400 spectrometer at 400 MHz or a Bruker AV200 spectrometer at 200 MHz. Chemical shifts ( $\delta$ ) are measured in parts per million. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Thin Layer Chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F<sub>254</sub> silica gel, and visualized using UV light (254 nm and 365 nm). Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. Electron impact (EI) mass spectra were carried out on a ThermoQuest MAT95XP mass spectrometer using ionisation energy of 70 eV and employing PerFluoroKerosene (PFK) as a reference sample. Electrospray (ES) mass spectra were carried out on a Thermo scientific Q-Exactive FTMS. UV–vis absorption spectra were recorded using a Hewlett Packard HP 8453 diode array spectrometer. Fluorescence spectra were measured using a Perkin Elmer LS50B fluorimeter.

### 2.3. Electrochemical measurements

PESA measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates. Electrochemical measurements were carried out using a PowerLab ML160 potentiostat interfaced via a PowerLab 4/20 controller to a PC running E-Chem for Windows Ver. 1.5.2. The measurements were run in argon-purged dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The cyclic-voltammograms were recorded using a standard three electrode configuration with a glassy carbon (2 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire pseudo reference electrode. The silver wire was cleaned in concentrated nitric acid followed by concentrated hydrochloric acid and then washed with deionized water. Cyclic-voltammograms were recorded with a sweep rate of 50 mV s<sup>-1</sup>. All the potentials were referred to the E<sub>1/2</sub> of ferrocene/ferrocenium redox couple.

### 2.4. Device fabrication and characterization of field effect transistors

A doped ( $N \sim 3 \times 10^{17}$  cm<sup>-3</sup>) silicon (Si) wafer was used as a substrate and as gate electrode. Discrete bottom contact OFETs were fabricated on thermally grown smooth silicon dioxide (SiO<sub>2</sub>)

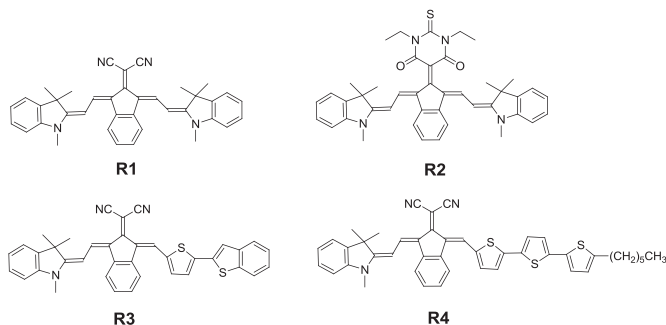


Fig. 1. Chemical structures of the new organic materials investigated in this work.

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