
List of Conferences Attended

1. Poster presented at “19th CRSI National Symposium in Chemistry” held at Department of Chemistry, University of North Bengal during 14th -16th July, 2016.
2. Poster presented at “National Seminar on Structure and Chemistry of Materials” held at Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda on 15th October, 2016. **(Best Poster Award)**
3. Poster presented at “National Conference on Chemistry of Materials and Biologicals 2018” held at Indian Institute of Technology (IIT), Gandhinagar during 4th and 5th January, 2018. **(Best Poster Award)**
4. Poster presented at “7th All Gujarat Research Scholars’ Meet” organized by Indian Chemical Society, Vadodara Chapter, held at Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda on 25th February, 2018. **(Best Poster Award)**
5. Poster presented at “International Conference on Energy and Environmental Challenges (CE2C)-2019” held at Visveswaraya National Institute of Technology (VNIT), Nagpur during 18th-19th January, 2019.
6. Poster presented at “Organic Molecules As Synthons & Reagents For Innovations (OMSRI)-2019” held at Indian Institute of Technology (IIT), Roorkee during 8th-10th February, 2019. **(Best Poster Award)**

List of Publications

1. Viraj J. Bhanvadia, Heta A. Patel, Neha N. Sharma, and Arun L. Patel*, “Synthesis, photophysical, electrochemical and single-crystal X-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile”, *Synthetic Communications*, **2016**, 46, 1052-1061.
2. Viraj J. Bhanvadia, Yash J. Mankad, Arun L. Patel*, and Sanjio S. Zade*, “Synthesis, characterization and electrochemistry of polycyclic fused aromatic pyrroles and their conjugated polymers”, *New J. Chem.*, **2018**, 42, 13565-13572.
3. Viraj J. Bhanvadia, Arun L. Patel*, and Sanjio S. Zade*, “Constructing a self-assembling C₃-symmetric covalently linked (fused) donor-acceptor-type molecule containing a hexazatriphenylene core”, *New J. Chem.*, **2018**, 42, 17700-17707.

Synthesis, photophysical, electrochemical and single-crystal x-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile

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ABSTRACT

The optical characteristics, redox properties, thermogravimetric stability and single-crystal X-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile are examined using ultraviolet–visible spectrophotometry, cyclic voltammetry, thermal gravimetric analysis–diffraction scanning calorimetry analysis, single-crystal X-ray diffraction and density functional theory calculations. Evidently, the crystal structure of compound **6** is sustained by a number of weak nonconventional intermolecular forces of attraction such as C-H...N, C-H... π donor–acceptor interactions.

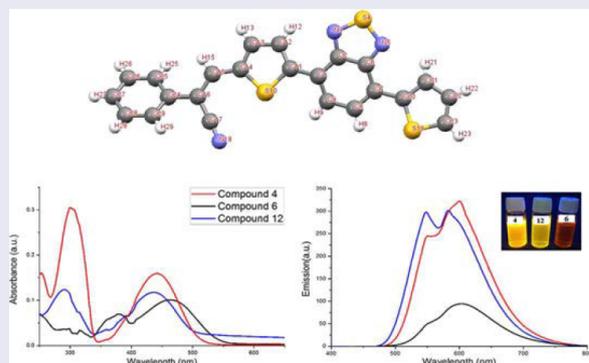
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GRAPHICAL ABSTRACT



Introduction

2,1,3-Benzothiadiazole (BTD) derivatives are outstanding compounds because of their electron-withdrawing properties and have been used as units of electron acceptors for conducting materials.^[1] BTD containing compounds are expected to afford well ordered

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Synthesis, characterization and electrochemistry of polycyclic fused aromatic pyrroles and their conjugated polymers†

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Polycyclic fused aromatic pyrrole-based compounds, benzodipyrrole, naphthobipyrrole and their alkylated derivatives, were synthesized and studied electrochemically. Amongst these, naphthobipyrrole having a tetracyclic fused aromatic structure was electrochemically polymerized to give the homopolymer of naphthobipyrrole, poly(naphthobipyrrole), indicating good reactivity of α,α' -pyrrolic positions towards oxidative coupling. As a strategic approach towards the synthesis of copolymers, naphthobipyrrole was copolymerized with arylaldehyde to afford poly(arylmethylene naphthobipyrrole) by exploring the reactivity of β,β' -pyrrolic positions. Moreover, optical and electrochemical studies showed that the copolymer possessed a low optical bandgap and an elevated HOMO level. The scan rate dependent cyclic voltammetry studies of the copolymer film showed the formation of an electroactive material.

1. Introduction

Conjugated polymers have attracted considerable attention due to their simple and cost-effective processability.^{1,2} Additionally, the electronic and optical properties of conjugated polymers can be tuned *via* molecular engineering.^{2,3} Conjugated polymers, such as poly(*p*-phenylene), polyaniline, polythiophene and pyrrole, having benzenoid or heterocyclic units, have been used in various organic electronic devices.⁴ Among these conjugated polymers, polypyrroles have been used for many commercial applications like functional membranes, electrochromic windows and displays,^{5–8} solid electrolytic capacitors, solid-state 'batteries', anti-electrostatic coatings, wires, microactuators, biosensors, gas sensors, *etc.* because of their high conductivity and facile synthesis.^{9,10} Pyrrole has a significantly lower oxidation potential than other five membered aromatic heterocycles like thiophene and furan.¹¹ As a result, pyrrole derivatives have been used as monomers for the synthesis of various conjugated polymers.^{3,4,10–14}

Different strategies have been adopted for the synthesis of π -conjugated polymers to obtain the desired properties of the resulting polymer. One of the strategies includes the synthesis of regioregular polymers which leads to a defect-free, structurally homogeneous head-to-tail coupled polymer with enhanced π -conjugation and improved electronic and optical properties.

Another important strategy is the synthesis of alternate donor-acceptor copolymers using various C–C coupling reactions. The third strategy is the introduction of fused aromatic rings into the conjugated polymer backbone. This is an important strategy to achieve high charge mobility for conjugated systems.^{15,16} Fused ring conjugated scaffolds endorse a planar and more rigid polymer backbone, which, in turn, leads to enhanced effective π -conjugation, reduces chain-folding and lowers the band-gap. The rigid fused ring conjugated structure lowers the reorganization energy of the polymer, which facilitates intermolecular hopping and charge carrier mobility.^{17,18}

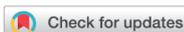
McCullough and co-workers used planar *N*-alkyldithienopyrroles as a fused aromatic building block and soluble substituted thiophenes for developing a series of novel electroactive and photoactive conjugated copolymers with a lower band-gap and higher conductivities.¹⁶ Swager and co-workers reported the facile synthesis of fused polycyclic aromatic pyrrole-based conjugated polymers from 1,2-di(3-pyrrolyl)benzene using a tandem cyclisation/polymerization strategy.¹³ The resulting conjugated polymer, poly(naphthobipyrrole), revealed a new class of robust, electrochromic conducting polymers having planarity and good π -conjugation along the polymer backbone, derived from the aromatic fused ring structure.

We hereby report the synthesis and electrochemical behaviour of a series of polycyclic fused aromatic pyrrole-based building blocks, benzodipyrrole **1**, *N,N'*-dioctylbenzodipyrrole **2**, *N,N'*-dioctyl-3-octylbenzodipyrrole **3**, naphthobipyrrole **4** and *N,N'*-dioctylnaphthobipyrrole **5** (Fig. 1). These polycyclic fused aromatic pyrrole-based building blocks show preponderant reactivity at carbons 3 and 8 (*i.e.*, the β and β' -pyrrolic positions)

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Constructing a self-assembling C_3 -symmetric covalently linked (fused) donor–acceptor-type molecule containing a hexaazatriphenylene core†

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A C_3 -symmetric covalently linked (fused) molecule, HAT-IPN, comprising a 13 fused ring system was synthesized by a condensation-cyclisation reaction between hexaazatriphenylenehexacarboxylic acid trisanhydride and 4,5-diamino-1,2-dioctyloxybenzene. This fused system exhibits ambipolar behaviour due to an n-type HAT-core at the center and three outer p-type fused dialkoxybenzimidazole moieties, which is confirmed by cyclic voltammetry. The self-assembling nature of this disc-shaped donor–acceptor type system is evident in ^{13}C NMR spectroscopy, dynamic light scattering studies, differential scanning calorimetry and atomic force microscopy (AFM) images, which illustrate the formation of the one-dimensional aggregates both in solution and in the film state; indicating its potential as an active component in organic electronic devices.

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1. Introduction

Fused polycyclic aromatic cores demonstrating extended π -conjugation have gained significant attention in the field of organic electronics.¹ Many linear and star-shaped molecules comprising a polycyclic aromatic core and extended π -conjugation have been identified as active components in optoelectronic devices^{2–4} due to their adequate HOMO and LUMO energy levels,^{5,6} isotropic absorption properties and strong tendency to assemble into quasi-1D columns which in turn help to generate a preferred charge transport pathway.⁷ The n-type and p-type semiconducting aromatic molecules have a tendency to form columnar-type π -stacked structures and self-assembled one-dimensional aggregates and demonstrate prominent possibilities as electron and hole transporting materials^{8–13} compared to glassy-type amorphous aromatics which show unfavourable positional and energy disorder.¹⁴

Recently, 1,4,5,8,9,12-hexaazatriphenylene (HAT) and its extended derivatives have been demonstrated to be good n-type semiconducting materials.^{3,10,15} These HAT-based materials, when properly substituted, show self-assembling behaviour both in solution and in the bulk state to form one-dimensional columnar-type aggregates.^{7,10,15–18} Although having self-assembling nature, most of these reported large polycyclic aromatic molecules either show n-type or p-type semiconducting characteristics.

The construction of electron donor–acceptor ensembles capable of transporting electrons and holes at the same time is important for their application in organic field effect transistors (OFETs) and organic light emitting field effect transistors (OLETs).^{19–21} Charge transfer complexes containing alternating donor–acceptor stacks exhibit high order geometry.²² The prime requirement for building highly ordered donor–acceptor assemblies is a strong interaction between electron donor–acceptor pairs as a result of complementary electronic characters. Such well-known pairs are bipyridinium²² or aromatic diimide^{23–27} as acceptors and dioxyarenes^{23–30} or tetrathiafulvalene^{28,30–33} (TTF) as donors. Klivansky *et al.* have reported one of such highly ordered donor–acceptor (D–A) assemblies using HAT-triimide as an electron acceptor and hexaalkoxytriphenylene as an electron donor utilizing the π - π interaction between the D–A pairs. Regardless of the advances in these self-assembly systems, breakthroughs in new material development are largely limited by the scarcity of the strongly interacting donor–acceptor pairs.¹⁵

An alternate approach to this is to construct D–A system by conjugating electron-rich groups with electron deficient groups, which can then self-assemble into columns, thereby forming a single molecule that is proficient in showing both n-type and p-type behaviour. One of these types of D–A systems has recently been reported by Blas-Ferrando *et al.*,⁷ in which a large star-shaped D–A system has been synthesized utilizing the n-type hexaazatriphenylene group fused with three p-type phthalocyanine units and this system exhibits a strong tendency to aggregate both in solution and in bulk.⁷ Herein, we report the construction of a C_3 -symmetric covalently linked donor–acceptor-type molecule in which the n-type hexaazatriphenylene core has been fused with three p-type di-amino-di-alkoxybenzene moieties by an

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