List of publications and papers presented in conferences

List of Publications

The research papers published based on work presented in this thesis:

1. **V. Kadam**, P. Bhatt, H. Karmakar, S. Zade and A. Patel, 2019. Benzimidazole-Substituted Indolo [3, 2-b] carbazoles: Acid-Responsive Probes. *ChemistrySelect*, *4,* (13), pp.3948-3952.
2. **V. Kadam**, A. Patel and S. Zade, 2016. Single precursor for the synthesis of donor and acceptor units of the low band gap polymers: Synthesis of benzodithiophene and thienopyrroledione from maleic anhydride. *Tetrahedron Lett*., *57*, (24), pp.2608-2611.
3. **V. Kadam**, S. Shaikh and A. Patel, 2016. A series of 2, 4, 5-trisubstituted oxazole: Synthesis, characterization and DFT modelling. *J. Mol. Struct*, 1114, pp.181-188.

List of conferences

1. Dialkyl thiophene dicarboxylate –Carbazole and dialkyl tert-thiophene dicarboxylate based π-conjugated Polymer: Synthesis, Characterization and Comparative study, **Vinay S. Kadam**, Arun L Patel, Sanjio S Zade, 23rd CRSI National Symposium in Chemistry (CRSI NSC-23), Indian Institute of Chemical Science and Research, Bhopal, July 13-15, 2018 (Poster Presentation).

2. Synthesis of benzodithiophene based molecules, important building blocks for the conjugated polymers, from dimethyl thiophene-3,4-dicarboxylate, **Vinay S Kadam**, **Arun L Patel** and Sanjio S Zade**,** National Seminar on Frontier Areas in Chemical Sciences, Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, March 19, 2016.(**Best Poster Presentation**).

3. An Efficient Synthetic Methodology for the Synthesis of Benzo[1,2-b:4,5-b']dithiophene (Donor) and Thieno[3,4-c]pyrrole-4,6-dione (Acceptor) derivatives *via* Single Precursor, **Vinay S Kadam**, Arun L Patel and Sanjio S Zade, National Conference on Recent Trends in Science of Materials, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, December, 28-30, 2015.(Poster Presentation)

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Chemistry SELECT Full Papers

Organic & Supramolecular Chemistry

Benzimidazole-Substituted Indolo[3,2-*b*]carbazoles: Acid-Responsive Probes

Vinay S. Kadam,[a] Prachi A. Bhatt,[a] Himadri S. Karmakar,[b] Sanjio S. Zade,*[b] and Arun L. Patel*[a]

Benzimidazole substituted indolo[3,2-*b*]carbazole derivatives (**5** and **6**) were synthesized by formylation of *N*,*N*'-dioctylindolo [3,2-*b*]carbazole followed by reaction with *o*-phenyelene diamine. The structures of these two compounds were characterized by high resolution mass-spectrometry (HRMS) and NMR (^{1}H and ^{13}C) spectroscopy. Their photophysical and electrochemical properties were studied by absorption and emission spectroscopy and cyclic voltammetry. Compounds **5** and **6** showed sensitivity towards acid in solution as well as in the solid state. Density functional theory (DFT) studies showed that compound **5** is more planar compared to **6**. Frontier molecular orbitals (FMO) analysis suggested that photoinduced electron transfer (PET) from indolo[3,2-*b*]carbazole moiety (fluorophore) to the protonated benzimidazole unit results in quenching.

Introduction

Indolo[3,2-*b*]carbazole (ICZ) has shown remarkable application in fields of medicinal, biological and material sciences.[1] ICZ derivatives are known for their significantly planar and rigid conjugated structures which are analogous to pentacene in terms of planarity and shows remarkable photophysical properties. The alkylation of nitrogen atoms in ICZ improves its solubility in organic solvent.[2] Some of the ICZ derivatives were found suitable as active material in organic field-effect transistors (OFETs).[3,4] Several ICZ derivatives were used as luminescence and hole-transporting materials[5] in the organic light emitting diodes (OLEDs).

Benzimidazole derivatives have been widely exploited in the field of sensors, especially as emissive sensor.[6] Recently, numerous benzimidazole derivatives have been reported as chemosensor,[7] fluorescent anion receptors[8] ratiometric fluorescent acid probes[9] and fluoride sensor[10] by various research groups. Among those, carbazole-benzimidazole based sensor[11] showed high and reversible sensitivity for volatile acid vapors. Carbazole derivatives were extensively studied as an active material for OLED, OFET devices[12] as well as in bio-imaging applications.[13]

ICZ unit possesses confined planar conformation which causes certain restriction in molecular rotation. ICZ unit substituted with benzimidazole ring systems can also enhanced the rigidity. The radiation less decay of excited states results from the intramolecular vibrations can be lowered by combined effects achieved from ICZ and benzimidazole units. Carbazole-benzimidazole based molecules[11] and several other molecules were widely used as a fluorescent sensors for detection of protons and metals, where fluorescence of the probes is quenched by the analyte; in several applications,[14] especially for the intracellular imaging.[15]

Herein, we report the synthesis of two new dialkyl ICZ-benzimidazole derivatives, 2-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-Indolo[3,2-*b*]carbazole (**5**) and 6-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-Indolo[3,2-*b*]carbazole (**6**). Both compounds showed bright fluorescence in their solution. The emission property of these compounds exploited to detect strong organic acids such as trifluoroacetic acid (TFA). We have also explored emission property of these compounds for other organic acids such as triflic acid and *p*-toluene sulfonic acid.

Results and Discussion

Synthesis of compound 5 and 6

Formylated indolo[3,2-*b*]carbazoles **3** and **4** were synthesized as showed in the scheme 1. Compound **1** was synthesized by following procedure reported by Bergman *et al.*[16] Compound **1** was alkylated with octyl bromide in presence of NaOH to afford compound **2**. Formylation of compound **2** by Vilsmeier-Haack reaction afforded 5,11-dioctyl-indolo[3,2-*b*]carbazole-2-carbaldehyde (**3**) and 5,11-dioctyl-indolo[3,2-*b*]carbazole-6-carbaldehyde (**4**) (Scheme 1)[4] in 3:7 ratio, which were separated by column chromatography. Compounds **3** and **4** were reacted with *o*-phenylene diamine in dry dimethyl formamide (DMF) in presence of *p*-toluene sulfonic acid (*p*-TSA) at elevated temperature to yield corresponding benzimidazole-substituted ICZ **5** and **6** (Scheme 2).

[a] *V. S. Kadam, P. A. Bhatt, Dr. A. L. Patel*
Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390 002, Gujarat, India
E-mail: arunpatel_5376@yahoo.co.in
[b] *H. S. Karmakar, Dr. S. S. Zade*
Department of Chemical Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur-741252, Nadia, West Bengal, India
E-mail: sanjiozade@iiserkol.ac.in

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Single precursor for the synthesis of donor and acceptor units of the low band gap polymers: synthesis of benzodithiophene and thienopyrroledione from maleic anhydride

Vinay S. Kadam [a], Arun L. Patel [a,*], Sanjio S. Zade [b,*]

[a] Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390 002, India
[b] Department of Chemical Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur 741252, Nadia, West Bengal, India

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Donor–acceptor conjugated polymers

ABSTRACT

An efficient route was developed to synthesize dimethyl thiophene-3,4-dicarboxylate from maleic anhydride. Dimethyl thiophene-3,4-dicarboxylate was used as a single precursor for synthesis of benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) and Thieno[3,4-*c*]pyrrole-4,6-dione (TPD) derivatives. BDT and TPD derivatives have been highly exploited as donor and acceptor units, respectively, to synthesize important donor–acceptor (D–A) conjugated polymers. BDT-based polymers were found to be one of the most efficient conjugated polymers for organic photovoltaic application. Synthesis of quinone precursor of the dihydroxybenzothiophene was accomplished by a new and unconventional methodology which includes reaction of 3,4-thiophene dicarboxylate with sodium hydride in THF. Dithienobenzoquinone dicarboxylate and dihydroxybenzodithiophene dicarboxylate were characterized structurally by single-crystal X-ray diffraction. Both compounds show strong π-stacking interaction and arrange in the parallel molecular sheets in the crystals.

Introduction

Conjugated polymers have attracted significant research interest because of their applications in organic electronic devices such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs).[1] Among them organic photovoltaic devices are often seen as inexpensive, greener, and renewable alternate energy sources to that of the conventional ones.[2] The light weight, flexibility and ability to cast them over large area are described as their advantages.[3]

The donor–acceptor concept[4] has been greatly exploited in the conjugated polymers to tune the electronic and structural properties.[5] The thiophene-fused ring systems in the conjugated polymer backbone possess several advantages. Such thiophene-fused conjugated systems exhibit extended π-conjugation along with structural rigidity in the conjugated polymer. These factors improve the intermolecular interaction in the solid films as well as lower the band gap of the polymers. The flat π-systems improve charge transport properties as well as they increase quinoidal character of the conjugated systems which leads to lowering of the bandgap. Benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) are examples of thiophene-fused ring systems which are among the most explored building blocks of conjugated polymers.

BDT-based molecules have emerged as prominent building blocks for conjugated systems in the number of organic electronic applications.[6] Initially, these conjugated systems were used as active materials in OFETs.[7,8] In recent years, these building blocks were used to construct donor conjugated systems for OPV devices.[9,10] The power conversion efficiencies of the OPV devices using conjugated systems comprising BDT unit have exceeded 8%.[11,12] Conjugated systems comprising the symmetric, rigid, and highly planar BDT unit showed better charge mobility due to presence of efficient π-stacking interaction. Alkoxy substituents at the 4,8-positions of BDT improve the solubility of the resulting polymers without steric hindrance in the conjugation. Recently two dimensional conjugations on BDT units have been reported where the BDT has been functionalized through two perpendicular directions.[13] TPD has been considered as an excellent acceptor unit in the synthesis of low band gap polymers.[14] TPD have distinct benefit of lower energy bands resulted from stabilization energy acquired from the formation of a quinoidal thiophene-maleimide species in their excited state. *N*-Substitution of alkyl groups

* Corresponding authors.
E-mail addresses: arunpatel_5376@yahoo.co.in (A.L. Patel), sanjiozade@iiserkol.ac.in (S.S. Zade).

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A series of 2, 4, 5-trisubstituted oxazole: Synthesis, characterization and DFT modelling

Vinay S. Kadam, Saminaparwin G. Shaikh, Arun L. Patel*

Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390 002, India

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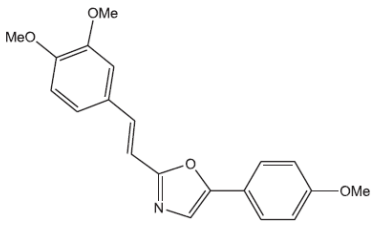
ABSTRACT

A new series of 2,4,5-trisubstituted oxazole were synthesized with good yields using simple methodology. All the compounds were thoroughly characterized by IR, NMR (^{1}H and ^{13}C) and mass spectrometry and structures of 2-(4-butyloxyphenyl)-4,5-dimethyloxazole (**5b**) and 4,5-dimethyl-2-(4-(octyloxy) phenyl)oxazole(**5e**) were unambiguously determined by X-ray crystallography. Evidently, the crystal structures of these compounds showed C–H···N and C–H···O intermolecular interactions. The electronic structures of these compounds were also studied by DFT at B3LYP/6-311G ++ level of theory.

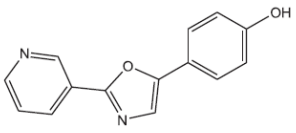
1. Introduction

Oxazoles have been found as subunits in numerous natural products [1]. Oxazole is also a valuable precursor in various biochemical as well as synthetic transformations [2–5].

Numerous pharmacologically important compounds used as antibiotics and antiproliferatives contain oxazole ring systems. Some very important derivatives of 2,5-diaryloxazoles, such as annuloline (from *Loliummultiflorum*) [6] and halfordinol (from *Halfordiascleroxyla*) [7] have been isolated from plant sources and have also been prepared in the laboratories. Annuloline was the first demonstration of the oxazole ring in nature.



annuloline



halfordinol

* Corresponding author.
E-mail address: arunpatel_5376@yahhoo.co.in (A.L. Patel).

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