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# The first generation and trapping of a five-membered ring allene: 2-dehydro-3a,4,5,6,6a-pentahydropentalene

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Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey Received 15 January 2002; revised 19 February 2002; accepted 8 March 2002

Abstract—3-Bromo-3-fluorotricyclo[3.3.0.0<sup>2,4</sup>]octane (8) was prepared by addition of bromofluorocarbene to bicyclo[3.2.0]hept-6-ene (5). Treatment of a solution of 8 in ether with MeLi in the presence of furan afforded the trapping product 11. The formation of the trapping product is consistent with the first generation of a five-membered ring allene, namely, 2-dehydro-3a,4,5,6,6a-penta-hydropentalene (4), a reactive intermediate. © 2002 Elsevier Science Ltd. All rights reserved.

1- The first generation and trapping of a fivemembered ring allene: 2-dehydro-3a,4,5,6,6apentahydropentalene

# Addition of dibromocarbene to cyclobutene: characterisation and mechanism of formation of the products

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Cyclobutene reacted with dibromocarbene in solution to give 1,5-dibromocyclopent-1-ene (9), 1,2,6,6-tetrabromobicyclo[3.1.0]hexane (10), and 1,2,3,6-tetrabromocyclohex-1-ene (11), in a ratio of 1:4:8, respectively. Compounds 10 and 11 were found to be formed from a second carbene addition and rearrangement under the given reaction conditions.

Keywords: carbene, carbene addition, cyclopropane, cyclobutene

2- <u>Addition of dibromocarbene to cyclobutene:</u> <u>characterisation and mechanism of formation of the products</u>



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Tetrahedron

# Functionalization of saturated hydrocarbons. High temperature bromination of octahydropentalene. Part 19<sup>★</sup>

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Available online 28 September 2005

Abstract—The synthesis and thermal bromination of octahydropentalene was studied. The reaction afforded 1a,3a,4b,6b-tetrabromo-1,2,3, 4,5,6-hexahydropentalene (14) with remarkable regio- and stereospecificity. The structure of the product was determined by <sup>1</sup>H and <sup>13</sup>C NMR data and single X-ray structural analysis. The treatment of octahydropentalene with tenfold bromine gave the octabromopentalene derivative. The formation mechanism of the products is discussed.

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3- <u>Functionalization of saturated hydrocarbons. High</u> <u>temperature bromination of octahydropentalene.</u>

<u>Part 19</u>

# Bromofluorocarbene addition to 6-phenylbicyclo[3.2.0]hept-6-ene: characterization and formation mechanism of the products

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# Abstract

Bromofluorocarbene addition to 6-phenylbicyclo[3.2.0]hept-6-ene provided fluoro-indanes such as 4,6-difluoro-5-phenylindane, 5,6-difluoro-4-phenylindane, 5,7-difluoro-4-phenylindane, 4-bromo-6-fluoro-5-phenylindane and 5-bromo-6-fluoro-4-phenylindane. The characterization the formation mechanism of the products are discussed.

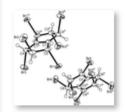
4- <u>Bromofluorocarbene addition to 6-</u> <u>phenylbicyclo[3.2.0]hept-6-ene: characterization and</u> <u>formation mechanism of the products</u> home archive editors for authors for readers submit open access



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A 1:1 cocrystal of (1R,3S,4S,6R)-1,2,3,4,5,6-hexabromo-1,2,3,4,5,6-hexahydrop (1R,2R,4S,5S)-1,2,3,4,5,6-hexabromo-1,2,4,5-tetrahydropentalene

T. Hökelek, D. D. Günbas, F. Algi and M. Balci

The components of the title compound, C<sub>8</sub>H<sub>6</sub>Br<sub>6</sub> and C<sub>8</sub>H<sub>4</sub>Br<sub>6</sub>, are hexa- and tetrabromopentalene derivativ treatment of hexahydropentalene with a tenfold excess of bromine. The asymmetric unit consists of two ha centres of symmetry are located at the mid-points of the central C=C and C-C bonds. The repulsive interact affect the molecular geometry.

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5- A 1:1 cocrystal of (1R,3S,4S,6R)-1,2,3,4,5,6-hexabromo-1,2,3,4,5,6-hexahydropentalene and (1R,2R,4S,5S)-1,2,3,4,5,6-hexabromo-1,2,4,5-tetra-<u>hydropentalene</u>

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# Simple, Mild, and Efficient Method for the Reduction of 1,4-Benzoquinones to Hydroquinones by the Action of NaN<sub>3</sub>

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**Abstract:** A simple, mild, and efficient method is presented for the reduction of 1,4-benzoquinones to hydroquinones by the action of NaN<sub>3</sub> under neutral conditions in the presence of water.

6- <u>Simple, Mild, and Efficient Method for the</u>
Reduction of 1,4-Benzoquinones to Hydroquinones by
the Action of NaN<sub>3</sub>







Electrochimica Acta 53 (2008) 2574-2578

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# A processable rainbow mimic fluorescent polymer and its unprecedented coloration efficiency in electrochromic device

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Received 20 August 2007; received in revised form 2 October 2007; accepted 14 October 2007 Available online 22 October 2007

Dedicated to Professor Ahmet M. Önal.

# Abstract

A processable rainbow mimic fluorescent polymer (PSNSF) based on 1-(9H-fluoren-2-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNSF) was synthesized via electrochemical polymerization in a mixture of ethanol and CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M LiClO<sub>4</sub>. Characterization was carried out using cyclic voltammetry, UV-vis and FT-IR spectroscopic techniques. Also, an electrochromic device based on PSNSF was studied, which exhibits high coloration efficiency (CE), high redox stability (retaining 98.6% of its optical activity after 4000th switch) and very low response time (less than 0.5 s).

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Keywords: Polythiophene; Polypyrrole; Fluorene; Electrochromic device; Coloration efficiency

7- A processable rainbow mimic fluorescent polymer and its unprecedented coloration efficiency in electrochromic device



Journal of Electroanalytical Chemistry

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# An electrochromic and fluorescent polymer based on 1-(1-naphthyl)-2,5-di-2-thienyl-1H-pyrrole

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### Abstract

A novel polymer was synthesized by electrochemical polymerization of 1-(1-naphthyl)-2,5-di-2-thienyl-1H-pyrrole (SNS-1-NAPH). The corresponding polymer (PSNS-1-NAPH) was characterized by cyclic voltammetry, FT-IR and UV-vis spectroscopy. The polymer has a very well-defined and reversible redox process in both organic and aqueous solutions. Furthermore, it shows stable electrochromic behavior; yellow in the neutral state, green in the intermediate state and violet in the oxidized state. PSNS-1-NAPH is soluble in common solvents. Although SNS-1-NAPH is almost nonfluorescent, its polymer is a yellow and/or green light emitter.

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Keywords: Electrochemical polymerization; Polythiophene; Polypyrrole; Naphthalene

8- An electrochromic and fluorescent polymer based on 1-(1-naphthyl)-2,5-di-2-thienyl-1H-pyrrole



# Journal of Electroanalytical Chemistry

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A novel conducting polymer based on terthienyl system bearing strong electron-withdrawing substituents and its electrochromic device application

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#### ABSTRACT

A novel conducting polymer bearing strong electron-withdrawing substituents (EWS) directly attached to the 3,4-positions of the thiophene ring was synthesized by electrochemical polymerization of diethyl 2,5-di(thiophen-2-yl)thiophene-3,4-dicarboxylate (SSS-Diester). The polymer (PSSS-Diester) was characterized by cyclic voltammetry, FT-IR and UV-vis spectroscopy. The polymer has a reversible redox process and demonstrates a stable electrochromic behavior; reddish orange in the neutral state, brown in the intermediate state and green in the oxidized state. Optical density and response time of the dual-type electrochromic device based on PSSS-Diester were found to be 0.23 and 0.6 s at 623 nm, respectively. It is also noteworthy that the device shows good environmental and redox stability (i.e. 94% of the optical activity of the device retained after 500th switch).

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9- A novel conducting polymer based on terthienyl system bearing strong electron-withdrawing substituents and its electrochromic device application

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Tetrahedron Letters

# An electroactive polymeric material and its voltammetric response towards alkali metal cations in neat water

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Received 6 December 2007; revised 3 March 2008; accepted 27 March 2008 Available online 29 March 2008

Dedicated to Professor Metin Balci on the occasion of his 60th birthday

#### Abstract

The syntheses and characterization of a unique system based on thiophene, pyrrole and benzo-15-crown-5 (SNS-Crown) and its corresponding polymer (PSNS-Crown) are reported. Furthermore, selective, clear and reversible voltammetric responses of the conjugated polymer (PSNS-Crown) film towards the alkali series Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> in both neat water and organic media (ethanol) are described.

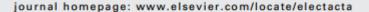
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Keywords: Chemosensor; Ion sensing; Crown ethers; Polythiophene; Polypyrrole

10- <u>An electroactive polymeric material and its</u> voltammetric response towards alkali metal cations in neat water



# Electrochimica Acta





# A new conducting polymer bearing 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) subunit: Synthesis and characterization

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### ARTICLE INFO

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#### ABSTRACT

A new monomer system based on thiophene, pyrrole and 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene dye (SNS-BODIPY) was synthesized and its corresponding polymer (PSNS-BODIPY) was obtained via repetitive cycling or constant potential electrolysis in 0.1 M tetrabutylammonium hexafluorophosphate dissolved in dichloromethane. The PSNS-BODIPY film has very stable and well-defined reversible redox couples during p-doping process. Multi-electrochromic polymer film has a band gap of 2.9 eV with two absorption bands in its neutral state at 351 and 525 nm, attributed to the polymer backbone and BODIPY subunits, respectively. The percentage transmittance changes between both states (neutral and oxidized) were found as 12.1% for 351 nm and 17.7% for 525 nm in the visible region as well as 46.2% for 1050 nm in the near-infrared region. Beyond the robustness, the PSNS-BODIPY film has high redox stability (retaining 53.3% of its electroactivity at 351 nm after 2000 switching) with a low response time of 1.0 s.

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11- A new conducting polymer bearing 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) subunit: Synthesis and characterization



# Electrochimica Acta

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# Processable electrochromic and fluorescent polymers based on *N*-substituted thienylpyrrole

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Electrochemical polymerization
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## ABSTRACT

A new series of processable conducting polymers based on thienylpyrrole was synthesized by electrochemical polymerization of 1-(1-naphthyl)-2,5-di(thiophen-2-yl)-1H-pyrrole, 1-(2-naphthyl)-2,5-di(thiophen-2-yl)-1H-pyrrole and 1-(benzo-15-crown-5)-2,5-di(thiophen-2-yl)-1H-pyrrole. The corresponding polymers have very well-defined and reversible redox processes in both organic and aqueous solutions. Furthermore, they exhibit multielectrochromic behavior: yellow in the neutral state, green and blue in the intermediate state and violet in the oxidized state. The polymer products are soluble in organic solvents and all of them are fluorescent.

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12- Processable electrochromic and fluorescent polymers based on N-substituted thienylpyrrole



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# A Novel Neutral State Green Polymeric Electrochromic with Superior n- and p-Doping Processes: Closer to Red-Blue-Green (RGB) Display Realization\*\*

By Atilla Cihaner\* and Fatih Algi\*

Two donor-acceptor systems, 4,7-di-2-thienyl-2,1,3-benzoselenadiazole (TSeT) and 4,7-di-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl-2,1,3-benzoselenadiazole (ESeE) are synthesized and electropolymerized to give polymers PTSeT and PESeE, respectively. One of the polymers, PTSeT, is blue-green in the neutral state and soluble, exhibiting a deep-red emission color. The other, PESeE, is the first 2,1,3-benzoselenadiazole-based neutral state green polymer with a narrow bandgap (1.04 eV). Furthermore, PESeE has superior and durable n- and p-doping processes. Beyond the stability and the robustness, both of the polymer films exhibit multi-electrochromic behavior.

13- A Novel Neutral State Green Polymeric
Electrochromic with Superior n- and p-Doping
Processes: Closer to Red-Blue-Green (RGB) Display
Realization

# DFT calculations of pentalenoquinones: towards the interception of 2-bromopentalene-1,5-dione

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This paper is dedicated to Professor Udo H. Brinker on the occasion of his 65th birthday

### Abstract

To reveal the stability and the aromatic character of pentalenoquinones (PQs) 1-4 and the corresponding bromo derivatives (Br-PQs) 6-9, DFT calculations (B3LYP/6-311+G(d,p)) concerning the geometry optimization, total energy and nucleus independent chemical shift (NICS) values were performed. It was found that all of the compounds have planar geometry. As the energy difference between HOMO-LUMO energy levels ( $\Delta \varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ ) and total energies were considered for the pentalene family, the stability order was found to be 1 > 2 > 3 > 4 for PQs, and 6 > 7 > 8 > 9 for Br-PQs. Furthermore 2-bromopentalene-1,5-dione (6) in solution was investigated and noted that it was too reactive to be isolated or even trapped.

Keywords: Pentalene, pentalenoquinones, DFT calculations

14- <u>DFT calculations of pentalenoquinones: towards</u> <u>the interception of 2-bromopentalene-1,5-dione</u>



# Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



# Electrochemical and optical properties of new soluble dithienylpyrroles based on azo dyes

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#### ABSTRACT

Two dithienylpyrroles based on azo dyes, namely 2,5'-dimethyl-[4-(2,5-di-thiophen-2-yl-pyrrol1-yl)-phenyl]azobenzene (SNS-AB2) and 2,5'-dimethyloxy-[4-(2,5-di-thiophen-2-yl-pyrrol1-yl)-phenyl]azobenzene (SNS-AB3), were synthesized and their corresponding polymers (PSNS-AB2 and PSNS-AB3) were successfully obtained via electropolymerization. The monomers have lower oxidation potentials (0.75 V and 0.80 V vs. Ag/AgCl for SNS-AB2 and SNS-AB3, respectively) when compared to their analogous. Both monomers exhibited photoisomerism properties under irradiation at 360 nm. During the irradiation process, for example, the color of SNS-AB3 changes from yellow to greenish yellow. The electroactive polymer films have well defined and reversible redox couples with a good cycle stability in both aqueous and organic solutions. The polymer films also exhibited electrochromic behaviors; color changes from yellowish green to dark green for the PSNS-AB2 ( $\lambda_{max}$  = 435 nm and  $E_g$  = 2.31 eV) and from mustard color to green for PSNS-AB3 ( $\lambda_{max}$  = 430 nm and  $E_g$  = 2.34 eV). Furthermore, the soluble polymers demonstrated different hues of yellow and green colors.

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15- <u>Electrochemical and optical properties of new soluble dithienylpyrroles based on azo dyes</u>



# Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react



# Synthesis and properties of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)-based conducting copolymers

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### ABSTRACT

The synthesis, characterization and engineering of a novel polymer based on a unique combination of 1,3,5,7-tetramethyl-8-(4-nitro-phenyl)-2,6-bis(2-thienyl)-4,4-difluoroboradiazaindacene and 3,4-ethylenedioxythiophene are highlighted. It was found that the polymer represents an environmentally robust electroactive material bearing high stability, well-defined quasi-reversible redox couple, and fast response time between redox states as well as high coloration efficiency.

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16- <u>Synthesis and properties of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)-based conducting copolymers</u>



# **Organic Electronics**





# An ambipolar low band gap material based on BODIPY and EDOT

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#### ABSTRACT

A novel donor–acceptor type conducting polymer based on BODIPY dye as acceptor and EDOT units as donor parts is synthesized electrochemically. The unique combination of BODIPY and EDOT units provides an ambipolar (n- and p-doping processes) low band gap material (4). This is the first example of p-n junction in an organic  $\pi$ -conjugated material where BODIPY unit is incorporated directly in the main chain. Furthermore, the polymer film exhibits electrochromic behavior upon p-doping: a color change from light violet (neutral) to indigo (oxidized).

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# 17- An ambipolar low band gap material based on BODIPY and EDOT

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PAPER 1341

# Synthesis of Novel 1,4-Benzoquinone-Containing 1,2,3-Triazoles: An Entry Into a New Library

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Abstract: A heretofore unexplored library of 1,4-benzoquinonecontaining 1,2,3-triazoles was prepared by the application of a highly regioselective copper(I)-catalyzed process. Furthermore, the utilization of this novel triazole–1,4-benzoquinone system as an interesting class of extended, branched molecules for the construction of new supramolecular architectures is presented.

Key words: benzoquinones, azides, triazoles, copper(I) catalysis, regioselectivity

the triazole moiety. Furthermore, the utilization of this novel triazole-quinone system as an interesting class of extended, branched molecules for the construction of new supramolecular architectures is presented here.

Our initial exploratory efforts involved the synthesis of the valuable 2-(azidomethyl)-substituted hydroquinone (2a) scaffold (see Scheme 1) which bears both the masked triazole functionality, obtainable through a copper(I)-catalyzed 1,3-dipolar cycloaddition, and the benzoquinone moiety, accessible through oxidation.

18- Synthesis of Novel 1,4-Benzoquinone Containing 1,2,3-Triazoles: An Entry Into a New Library.



# Organic Electronics





# An ambipolar neutral state green polymeric electrochromic

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#### Keywords: Conducting polymers Donor-acceptor Electrochromism RGB

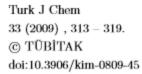
EDOT Quinoxaline

#### ABSTRACT

The synthesis and properties of highly stable neutral state green polymeric electrochromic, P1, which is based on 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(1H-pyrrol2-yl)quinoxaline were highlighted. P1 exhibits three well-defined absorption bands with a narrow band gap (1.17 eV). The n- and p-doping (ambipolar) processes suggest that P1 is one of the most promising neutral state green polymers and it can be used in supercapacitors as either cathode or anode electrode material. Apart from the stability and the robustness of the polymer film, P1 shows multi-electrochromic behavior; gray-purple in the reduced form and highly transmissive blue color in the oxidized state.

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# 19- An Ambipolar Neutral State Green Polymeric Electrochromic.





# The synthesis, characterization and energy transfer efficiency of a dithienylpyrrole and BODIPY Based Donor-Acceptor System

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A dithienylpyrrole-BODIPY based donor-acceptor system with 1,4-phenylene spacer as a model system for energy transfer was designed and synthesized. Absorption and emission spectra have revealed an efficient resonance energy transfer from dithienylpyrrole as donor to BODIPY as acceptor.

Key Words: Fluorescence Resonance Energy Transfer, Donor-Acceptor System, Dithienylpyrrole, BOD-IPY.

20- <u>The Synthesis, Characterization and Energy</u>
<u>Transfer Efficiency of a Dithienylpyrrole and</u>
<u>BODIPY Based Donor-Acceptor System.</u>



# Tetrahedron

journal homepage: www.elsevier.com/locate/tet



# Synthesis and properties of a novel redox driven chemiluminescent material built on a terthienyl system

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### ARTICLE INFO

#### Article history: Received 14 February 2009 Received in revised form 22 April 2009 Accepted 7 May 2009 Available online 13 May 2009

Keywords: Chemiluminescence Sensors Luminol Forensic science Conducting polymers

#### ABSTRACT

A novel redox driven chemiluminescent material built on a terthienyl system, namely 5,7-di-ethylenedioxythiophen-2-yl-2,3-dihydro-thieno[3,4-d]pyridazine-1,4-dione (ETE-Lum), which is soluble in both organic media and basic aqueous solution was synthesized and characterized. Furthermore, its polymer, PETE-Lum, which is one of the most rare examples of chemiluminescent polymeric materials bearing a pyridazine unit, was obtained successfully by electrochemical means. Both of the materials give chemiluminescence either by treatment with oxidants (H<sub>2</sub>O<sub>2</sub> and/or KMnO<sub>4</sub>) or by the application of a potential pulse.

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21- <u>Synthesis and Properties of a Novel Redox Driven</u>
<u>Chemiluminescent Material Built on a Terthienyl</u>
<u>System.</u>



# Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



# Electrochemical and optical properties of new soluble dithienylpyrroles based on azo dyes

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### ARTICLE INFO

# Article history: Received 5 August 2008 Received in revised form 27 September 2008 Accepted 29 September 2008 Available online 15 October 2008

Keywords: Electropolymerization Photoisomerization Polythiophene Polypyrrole Azobenzene

### ABSTRACT

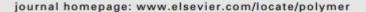
Two dithienylpyrroles based on azo dyes, namely 2,5'-dimethyl-[4-(2,5-di-thiophen-2-yl-pyrrol1-yl)-phenyl]azobenzene (SNS-AB2) and 2,5'-dimethyloxy-[4-(2,5-di-thiophen-2-yl-pyrrol1-yl)-phenyl]azobenzene (SNS-AB3), were synthesized and their corresponding polymers (PSNS-AB2 and PSNS-AB3) were successfully obtained via electropolymerization. The monomers have lower oxidation potentials (0.75 V and 0.80 V vs. Ag/AgCl for SNS-AB2 and SNS-AB3, respectively) when compared to their analogous. Both monomers exhibited photoisomerism properties under irradiation at 360 nm. During the irradiation process, for example, the color of SNS-AB3 changes from yellow to greenish yellow. The electroactive polymer films have well defined and reversible redox couples with a good cycle stability in both aqueous and organic solutions. The polymer films also exhibited electrochromic behaviors; color changes from yellowish green to dark green for the PSNS-AB2 ( $\lambda_{max}$  = 435 nm and  $E_g$  = 2.31 eV) and from mustard color to green for PSNS-AB3 ( $\lambda_{max}$  = 430 nm and  $E_g$  = 2.34 eV). Furthermore, the soluble polymers demonstrated different hues of yellow and green colors.

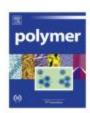
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22- Electrochemical and Optical Properties of Azo Dye Based Conducting Copolymer.



# Polymer





# A new low-voltage-driven polymeric electrochromic

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### ARTICLEINFO

# Article history: Received 9 August 2009 Received in revised form 2 November 2009 Accepted 4 November 2009 Available online 10 November 2009

Keywords: Conducting polymers Electrochromism Donor-acceptor system

### ABSTRACT

Design, synthesis, and properties of a novel donor-acceptor-donor type low-voltage-driven green polymeric electrochrome, P1, which is based on 8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-11-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)acenaphtho[1,2-b]quinoxaline (1) are highlighted. It is noted that P1 has an ambipolar (n- and p-doping processes) character in 0.1 M tetrabutylammonium hexafluorophosphate/dichloromethane solution and switches to a transmissive blue state upon oxidation. Furthermore, this new polymeric electrochromic candidate exhibits high redox stability, high coloration efficiency and/or contrast ratio, high percent transmittance (%T) and low response time (1.0 s) with a band gap of 1.10 eV-1.25 eV.

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# 23- <u>A New Low-Voltage-Driven Polymeric</u> Electrochromic.

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# Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



# A new soluble neutral state black electrochromic copolymer via a donor-acceptor approach

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### ARTICLE INFO

#### Article history: Received 22 March 2010 Received in revised form 30 April 2010 Accepted 1 May 2010 Available online 10 May 2010

Keywords: Electropolymerization Donor-acceptor approach Electrochromism Benzoselenadiazole Benzorriazole

#### ABSTRACT

Iwo donor-acceptor systems, 2-decyl-4,7-bis(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2H-benzo[d][1,2,3]triazole (1) and 4,7-bis(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2,1,3-benzoselenadiazole (2) are explored in order to attain a low bandgap black polymer electrochrome, which is highly difficult to attain due to the complexity of designing such materials. Electrochemical polymerization of 1 and z in 1:4 monomer feed ratio was performed in a mixture of acetonitrile and dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate. It was found that electropolymerization provides a processable neutral state black copolymer, (P(1-co-2)), which absorbs virtually the whole visible spectrum (400–800 nm). (P(1-co-2)) is the first low bandgap (1.45 eV) electropolymerized material, which switches from black color (L = 14.3, a = 0.29, b = 0.35) in the neutral state to transmissive grey (L = 39.2, a = 0.29, b = 0.33) in the oxidized state with 15.3% of the transmittance change at 522 nm. Furthermore, it exhibits excellent operational and/or environmental stability under ambient conditions.

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24- <u>A New Soluble Neutral State Black</u>
<u>Electrochromic Copolymer via a Donor-acceptor</u>
<u>Approach</u>.



# Donor-Acceptor Polymer Electrochromes with Tunable Colors and Performance

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To demonstrate the effect of donor (D) and acceptor (A) units on the structure-property relationships of electrochromic polymers, design, synthesis, characterization and polymerization of a series of D-A type systems, 1-5, based on thiophene, 3,4-ethylenedioxythiophene, and 3,3didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine as D units and 2,1,3-benzoselenadiazole, 2,1,3benzothiadiazole and 2-decyl-2H-benzo[d][1,2,3]triazole as A units are highlighted. It is found that these units play key roles on the redox behavior, band gap, neutral state color, and the electrochromic performance (stability, optical contrast, coloration efficiency, and switching time) of the system. It is noted that electropolymerization of these D-A systems provides processable low band gap electrochromes, P1-P5, exhibiting high redox stability, coloration efficiency, transmittance and/or contrast ratio and low response time. Furthermore, P1-P5 reflect various hues of blue and green pallets of the RGB color-space in the neutral state. In particular, it is noteworthy that P5 is an excellent blue-to-colorless polymeric electrochrome, which, to our best knowledge, exhibits the highest optical contrast and coloration efficiency among the D-A type systems. The panoramic breadth of the neutral state colors and intriguing features of these polymeric materials further confirm that D-A approach allows engineering tunable electrochromes, which hold promise for commercialization of polymeric RGB electrochromics.

# 25- <u>Donor-Acceptor Polymer Electrochromes with</u> <u>Tunable Colors and Performance.</u>

Full Paper ELECTROANALY

# A Diverse-Stimuli Responsive Chemiluminescent Probe with Luminol Scaffold and Its Electropolymerization

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## Abstract

A diverse-stimuli responsive chemiluminescent system, SNS-Lum, and its electropolymerization to give PSNS-Lum, which is the first example of conjugated polymers with pendant luminol arms inducing chemiluminescence in the presence of super oxide radical anion under neutral conditions, are highlighted.

26- A diverse-stimuli responsive chemiluminescent probe with luminol scaffold and its electropolymerization.



# **Organic Electronics**

journal homepage: www.elsevier.com/locate/orgel



# A neutral state yellow to navy polymer electrochrome with pyrene scaffold

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#### ARTICLE INFO

Article history: Received 15 April 2011 Received in revised form 18 May 2011 Accepted 21 May 2011 Available online 25 June 2011

Keywords: Donor-acceptor approach Electrochromism Fluorescence Pyrene ProDOT

#### ABSTRACT

A new pyrene based soluble polymer, namely poly(3,3-didecyl-6-(1-(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)pyren-6-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepine), P5, which is synthesized by both chemical and electrochemical methods, is highlighted. The polymer shows both electrochromic and fluorescent properties (the emission of yellow (545 nm) and yellowish green light (524 nm) in solid state and in THF solution, respectively). It is noteworthy that P5 has a specific optical band gap (2.2 eV) to reflect the yellow color in the neutral state. Furthermore, the optical and electrochemical features of the polymer were investigated.

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# 27- A Neutral State Yellow to Navy Polymer Electrochrome with Pyrene Scaffold.



# **Organic Electronics**

journal homepage: www.elsevier.com/locate/orgel



# Donor-acceptor polymer electrochromes with cyan color: Effect of alkyl chain length on doping processes

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### ARTICLE INFO

# Article history: Received 9 September 2011 Received in revised form 26 October 2011 Accepted 30 October 2011 Available online 21 November 2011

Keywords: Electrochromic polymers CMY colors ProDOT Benzothiadiazole

#### ABSTRACT

A new series of donor-acceptor-donor (D-A-D) type compounds consisting of dialkyl substituted 3,4-propylenedioxythiophene and benzothiadiazole units were synthesized and polymerized chemically and electrochemically to investigate the effect of alkyl chain length on the doping process of the conjugated polymers. It was found that the alkyl chain length plays a key role on both doping processes and the solubility of the polymer. It is also noteworthy that this new series of D-A-D electrochromes transmits or reflects the cyan color of the Cyan-Magenta-Yellow (CMY) color space in the neutral state which can be switched to transmissive grey when oxidized.

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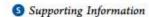
28- <u>Donor-Acceptor Polymer Electrochromes with</u>
<u>Cyan Color: Effect of Alkyl Chain Length on Doping Processes.</u>



# Members of CMY Color Space: Cyan and Magenta Colored Polymers Based on Oxadiazole Acceptor Unit

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ABSTRACT: In this study, three novel oxadiazole-based polymers were synthesized and their electrochemical and optical properties were investigated. The polymers were found to have both p- and n-type doping properties accompanied by electrochromic response. Two polymer films exhibit cyan and magenta colors, which constitute two legs of CMY color spaces, in their neutral states and they are soluble in common-organic solvents. According to the color mixing theory, all colors in the visible spectrum including black color can be obtained by using these polymers with a yellow colored electrochromic polymer. Among these polymers, the polymer bearing propyledioxythiophene donor units has some superior properties like high stability (it retains 94% of its electroactivity after 2000 cycles), solubility, and high coloration efficiency (230 cm²/C), whereas as expected ethylenedioxythiophene containing one has the lowest band gap as 1.08 eV.



29- Members of CMY Color Space: Cyan and Magenta Colored Polymers Based on Oxadiazole Acceptor Unit.

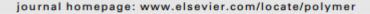
Department of Chemistry, Middle East Technical University, TR-06531 Ankara, Turkey

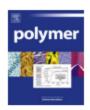
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# Polymer





# A novel terthienyl based polymer electrochrome with peripheral BODIPY

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### ARTICLE INFO

### Article history: Received 30 March 2012 Received in revised form 30 May 2012 Accepted 4 June 2012 Available online 13 June 2012

Keywords: Bodipy Terthienyl Electrochromic

#### ABSTRACT

Design, synthesis and electropolymerization of a new hybrid material based on terthienyl system bearing BODIPY appendage are reported. This electrochemically polymerized unique combination readily gives an electrochromic polymer with a narrow optical band gap (1.71 eV). The electrochrome exhibits purple color when neutralized and sky blue color when oxidized in a monomer-free electrolyte solution containing 0.1 M tetrabutylammonium tetrafluoroborate dissolved in acetonitrile. Spectroscopic and electrochemical features of the electroactive polymer electrochrome indicate that it is a promising candidate for electrochromic device and display applications.

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# 30- A novel terthienyl based polymer electrochrome with peripheral BODIPY.

# ChemComm

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# **COMMUNICATION**

# Triple channel responsive Cu<sup>2+</sup> probe†

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Received 6th July 2012, Accepted 29th August 2012 DOI: 10.1039/c2cc34842j

A simple, selective and sensitive  $Cu(\pi)$  probe is highlighted. It is noteworthy that this novel probe induces triple channel (colorimetric, fluorogenic and voltammetric) response to  $Cu(\pi)$  ions, which makes it viable for practical applications.

The design and synthesis of functional organic compounds that allow selective and sensitive detection of target metal ions have attracted considerable attention during the last two decades due to the fact that metal ions play essential and/or deleterious roles in biological and environmental processes. Among these ions, Cu<sup>2+</sup> is an important trace element which plays crucial roles in various biological processes. In addition to these crucial roles, Cu<sup>2+</sup> is a significant environmental pollutant and it has toxic effects on organisms especially at high concentration levels, since it can displace other metal ions

Scheme 1 Synthesis of 4.

# 31- Triple channel responsive Cu2+ probe.



# Tetrahedron Letters





# Synthesis of a novel on/off fluorescent cadmium(II) probe

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## ARTICLE INFO

Article history: Received 8 September 2012 Revised 10 October 2012 Accepted 18 October 2012 Available online 27 October 2012

Keywords: 1,10-Phenanthroline Cd(II) Fluorescence Bodipy

#### ABSTRACT

A novel on/off fluorescent Cd<sup>2+</sup> probe, which is based on a 1,10-phenanthroline scaffold with cofacial BODIPY units attached orthogonally as the receptor and fluorophore units, respectively, is described. The digital action of a two-input NOR logic gate is also demonstrated.

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# 32- Synthesis of a novel on/off fluorescent cadmium (II) probe.



# Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet



# Incorporation of a 2,3-dihydro-1H-pyrrolo[3,4-d]pyridazine-1,4(6H)-dione unit into a donor-acceptor triad: synthesis and ion recognition features $^{\star}$

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## ARTICLE INFO

Article history: Received 22 August 2012 Revised 26 September 2012 Accepted 18 October 2012 Available online 26 October 2012

Keywords: Dihydro-pyrrolo-pyridazine-dione Donor-acceptor Thiophene Ion recognition Copper(II) Fluorescence

# ABSTRACT

A novel directly-linked donor-acceptor-donor (D-A-D) type system, which is based on 2,3-dihydro-1*H*-pyrrolo[3,4-d]pyridazine-1,4(6*H*)-dione as the A unit and thiophene as the D units, respectively, is designed, synthesized, and characterized by spectroscopic methods. This novel D-A-D system can be used for the fluorogenic detection of Cu<sup>2+</sup> among other ions.

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33- Incorporation of a 2,3-dihydro-1H-pyrrolo[3,4-d]pyridazine-1,4(6H)-dione unit into a donor-acceptor triad: synthesis and ion recognition features.



# Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



# A new processable and fluorescent polydithienylpyrrole electrochrome with pyrene appendages

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### ARTICLE INFO

# Article history: Received 12 September 2012 Received in revised form 6 December 2012 Accepted 9 December 2012 Available online 19 December 2012

Keywords: Thiophene Pyrrole Pyrene Electrochromism Fluorescence

### ABSTRACT

A new hybrid compound, namely 1-(pyren-3-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-P), was polymerized via both chemical and electrochemical methods. Chemically obtained soluble polydithienylpyrrole (c-PSNS-P) bearing pyrene appendages is a homogeneous and uniform polymer with a number averaged molecular weight of 15,200 g/mol. The polymer exhibits both multi-electrochromic and fluorescent properties. Upon oxidation, the color of electrochemically obtained polymer (e-PSNS-P) changes from yellowish orange to greenish yellow and to green/blue and finally to blue. In addition, the polymer induces yellowish orange (564 nm) and bright orange emission (613 nm) in solution and solid states, respectively.

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34- <u>A New Processable and Fluorescent</u>

<u>Polydithienylpyrrole Electrochrome with Pyrene</u>

<u>Appendages.</u>



# Tetrahedron

journal homepage: www.elsevier.com/locate/tet



# Nonreaction-based fluorescent Au<sup>3+</sup> probe that gives fast response in aqueous solution



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#### ARTICLE INFO

### Article history: Received 17 September 2012 Received in revised form 2 December 2012 Accepted 17 December 2012 Available online 10 January 2013

Dedicated to Professor Metin Balci on the occasion of his 65th birthday

Keywords: Gold (III) Fluorescent probes Fluorescence 2,5-Dithienylpyrrole

#### ABSTRACT

The design and synthesis of a simple, selective and efficient turn-off fluorescent Au<sup>3+</sup> probe, namely, diethyl 1-phenyl-2,5-di(thiophen-2-yl)-1*H*-pyrrole-3,4-dicarboxylate (1), are highlighted. To our best knowledge, this is the first example of nonreaction-based fluorescent Au<sup>3+</sup> probes.

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35- Nonreaction-based fluorescent Au3+ probe that gives fast response in aqueous solution.



# Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



# A new electrochromic copolymer based on dithienylpyrrole and EDOT



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#### ARTICLE INFO

#### Article history: Received 9 December 2012 Received in revised form 29 January 2013 Accepted 30 January 2013 Available online 18 February 2013

Keywords: Multicolor electrochromism Camouflage Dithienylpyrrole EDOT

#### ABSTRACT

A new compound, namely diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (1), was copolymerized with 3,4-ethylenedioxythiophene (EDOT) via electrochemical method. The copolymer exhibits multicolor electrochromic property: It is found that the copolymer, poly(1-co-EDOT), has a specific optical band gap (1.71 eV) to reflect and/or transmit reddish brown color in the neutral state, and it can be switched to reddish orange, orange, yellowish green and blue colors upon oxidation in a low switching time (1.0 s). Importantly, these colors are essential for camouflage and/or full color electrochromic device/display applications. In addition to these, the obtained copolymer has a coloration efficiency of 173 cm²/C at 500 nm.

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# 36- A New Electrochromic Copolymer Based on Dithienylpyrrole and EDOT.



# Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



# Design and synthesis of new 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene based electrochromic polymers



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### ARTICLE INFO

Article history: Received 14 March 2013 Received in revised form 3 July 2013 Accepted 21 July 2013 Available online 8 August 2013

Keywords: Electrochemical polymerization Electrochromics Thiophene EDOT BODIPY

#### ABSTRACT

Design, synthesis, optical and electrochemical properties of two novel 4,4'-Difluoro-4-bora-3a,4a-diazas-indacene (BODIPY) based donor-acceptor compounds, 1 and 2, are reported in order to elucidate the structure-property relationships in BODIPY based materials. Importantly, these compounds provide opportunity to be used as crosslinkers, since they have three electroactive donor sides. Furthermore, these compounds are polymerized successfully via electrochemical polymerization. The corresponding polymers (P1 and P2) are also characterized by using electrochemical and optical methods in monomerfree electrolyte solutions. It is found that both polymers P1 and P2 exhibit reversible oxidation peaks with half wave potentials of 0.70 V and 0.98 V vs. Ag/AgCl, respectively, and they have low optical band gaps (1.88 eV for P1 and 1.72 eV for P2). It is also noted that the polymers exhibit multielectrochromic properties upon doping: P1 can be switched from pink color in the neutral state to blue color in the oxidized state and P2 can be switched from transmissive pink color when neutralized to transmissive blue color when oxidized.

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37- <u>Design and synthesis of new 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene based electrochromic polymers.</u>



# Tetrahedron

journal homepage: www.elsevier.com/locate/tet



# Design, synthesis, photochromism and electrochemistry of a novel material with pendant photochromic units



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# ABSTRACT

In the present work, the synthesis, photochromism and electrochemistry of a novel material 1, 1-(4-[3,4-bis(2,5-dimethyl-3-thienyl)cyclopent-3-en-1-yl]phenyl)-2,5-di-2-thienyl-1H-pyrrole, with pendant dithienylethene (DTE) photochromic units are described. It should be noted that the system 1 can be reversibly and efficiently switched between open (10) and closed (1c) states by light in both solution and in the solid poly(methyl methacrylate) matrix. It is also noteworthy that the two isomers (10 and 1c) of this novel system 1 can be smoothly polymerized on ITO by electrochemical means. Surprisingly, the DTE unit in 1 does not retain its photochemical switching properties after immobilization onto ITO. The morphology of the polymer film was investigated by AFM analysis. Furthermore, it was found that the polymer exhibited remarkable electrochromic features that can be switched from green in the neutral state to violet state under applied external potentials without disturbing the photochromic units.

38- Design, synthesis, photochromism and

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<u>electrochemistry of a novelmaterial with pendant photochromic units.</u>

### Category

Synthesis of Materials and Unnatural Products

### Key words

electrochromism

electropolymerization

photochromism

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Design, Synthesis, Photochromism and Electrochemistry of a Novel Material with Pendant Photochromic Units Tetrahedron 2014, 70, 5064–5072.

# Independent Dual-Switching Colors from Dithienylethene/Dithienylpyrrole

Significance: Despite the high utility of dithienylethene (DTT) groups for organic electronics applications, there are few reports to date of these structures being incorporated into conducting polymers. The reported material is not only conductive, but also displays independent photochromic and electrochromic behavior. The researchers were able to demonstrate that both phenomena are reversible under several different conditions. Comment: While both the open and closed monomer forms can be electropolymerized, it was found the DTT groups are 'locked' after polymerization. The researchers hypothesize that this is due to close packing of the polymer chains leading to steric hindrance. It is possible that copolymerization or blending with a different structure could permit DTT photoswitching again, as the monomeric structure was capable of photoswitching after codeposition with poly(methyl methacrylate).

39- <u>Independent dual-switching colors from dithienylethene/dithienylpyrrole.</u>



# Tetrahedron Letters

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# A novel dual channel responsive zinc(II) probe



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#### ABSTRACT

A novel compound, 1, which is based on a 1,10-phenanthroline scaffold with cofacial BODIPY units, is synthesized via a three-step reaction sequence. It is noteworthy that 1 can be utilized for both visual and turn-off fluorometric detection of Zn<sup>2+</sup> ions in aqueous acetonitrile solution. The fluorescence response is based on cation-mediated oxidative photoinduced electron transfer (PET). The digital action of a two-input NOR logic gate is also demonstrated.

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40- A novel dual channel responsive zinc(II) probe.

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Research Article

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# Synthesis, properties, and electrochemistry of a photochromic compound based on dithienylethene and ProDOT

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Abstract: The synthesis, photochromic features, and electrochemistry of a novel material based on dithienylethene (DTE) and 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (didecyl-ProDOT) units are described. It is noteworthy that 1,2-bis(5-(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2-methylthiophen-3-yl)cyclopent-1-ene can be efficiently switched between open and closed states by light in both solution and in the solid poly(methyl metacrylate) (PMMA) matrix. It is also found that the emission of this novel compound can be switched on and off upon irradiation.

41- <u>Synthesis</u>, <u>properties and electrochemistry of a photochromic compound based on dithienylethene and ProDOT.</u>



# Tetrahedron Letters





# A novel turn-off fluorescent Pb(II) probe based on 2,5-di(thien-2-yl) pyrrole with a pendant crown ether



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#### ABSTRACT

The synthesis, optical, and ion-sensing characteristics of a novel compound, 1, which is based on a 2,5-di(thien-2-yl)pyrrole scaffold with a 15-crown-5 unit, are reported. It is noteworthy that 1 can be utilized for turn-off fluorimetric detection of Pb(II) ions. The fluorescence response is based on cation-mediated reductive photoinduced electron transfer.

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42- A novel turn-off fluorescent Pb(II) probe based on 2,5-di(thien-2-yl)pyrrole with a pendant crown ether.





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# An imidazo-phenanthroline scaffold enables both chromogenic Fe(II) and fluorogenic Zn(II) detection†

Aykut Yoldas<sup>a</sup> and Fatih Algi\*b

A novel, simple and efficient dual channel probe built on an imidazo-phenanthroline scaffold with a boronic acid unit, viz. 3-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-v1)phenylboronic acid, is disclosed. It is found that this novel probe induces chromogenic and fluorogenic responses to Fe(v1) and Zn(v1) ions, respectively. To our best knowledge, this is one of the rare examples of dual channel responsive probes that can be used for visual detection of Fe(v1) and turn-on fluorogenic detection of Zn(v1) ions, simultaneously.

43- An Imidazo-phenanthroline Scaffold Enables
Both Chromogenic Fe(II) and Fluorogenic Zn(II)
Detection.

# Atomistic Engineering of Chemiluminogens: Synthesis, Properties and Polymerization of 2,3-Dihydro-Pyrrolo[3,4-d] Pyridazine-1,4-Dione Scaffolds

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Abstract Two chemiluminescent compounds containing 2,5di(thien-2-yl)pyrrole and pyridazine units, namely 5,7di(thiophen-2-yl)-2,3-dihydro-1H-pyrrolo[3,4-d]pyridazine-1,4(6H)-dione (5) and 6-phenyl-5,7-di(thiophen-2-yl)-2,3dihydro-1H-pyrrolo[3,4-d]pyridazine-1,4(6H)-dione (6), were successfully synthesized and electrochemically polymerized. The compounds have chemiluminescent properties and glow in the presence of hydrogen peroxide in basic medium. The intensity of the glow can be increased dramatically by using Fe3+ ions, hemin (1.0 ppm) or blood samples (1.0 ppm) as catalyst. The compounds 5 and 6 have one well-defined irreversible oxidation peak at 1.08 V and 1.33 V vs Ag/AgCl, respectively. Electrochemical polymerization of both 5 and 6 were carried out successfully by repeating potential scanning in the presence of BF3. Et2O in an electrolyte solution of 0.1 M LiClO<sub>4</sub> dissolved in acetonitrile. The electronic band gaps (Eg) of the polymers P5 and P6 were found to be 2.02 eV and 2.16 eV, respectively. On the other hand, the corresponding polymers are electroactive and exhibited electrochromic features.

Keywords Chemiluminescence · Pyridazine · Thiophene · 2,5-di(thien-2-yl)pyrrole · Electrochromism

## Introduction

Enormous effort has been devoted to the design and synthesis of novel stimuli responsive organic materials considering the fact that they can lead to a variety of advanced technological applications in the field of sensors [1], molecular electronics and photonics [2–4], memories [5], electrochromic materials [6–12], light emitting diodes [13, 14], photovoltaics [15, 16] and transistors [17–20]. Among the stimuli responsive organic materials, chemiluminogens [21, 22] represent an important

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44- Atomistic Engineering of Chemiluminogens: Synthesis, Properties and Polymerization of 2,3-Dihydro-Pyrrolo[3,4-d]Pyridazine-1,4-Dione Scaffolds



# Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



# Synthesis, chemiluminescence and energy transfer efficiency of 2,3-dihydrophthalazine-1,4-dione and BODIPY dyad



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### ABSTRACT

The design, synthesis and energy transfer efficiency of a new covalently linked molecular dyad 5, which consists of 2,3-dihydrophthalazine-1,4-dione and BODIPY scaffolds, are reported. It is noteworthy that dyad 5 can induce chemiluminescence upon treatment with alkaline  $\rm H_2O_2$  in the presence of Fe(III) ions. This reaction triggers chemiluminescence resonance energy transfer (CRET) from 2,3-dihydrophthalazine-1,4-dione unit to BODIPY fluorophore, which act as the donor and the acceptor components, respectively. To our best knowledge, this is the first example of a covalently linked molecular dyad consisting of chemiluminogenic 2,3-dihydrophthalazine-1,4-dione and BODIPY dye. Importantly, dyad 5 can provide a low energy emitting material via the chemiluminescence energy transfer (CRET), which covers almost the entire visible region (400 nm–700 nm) of the electromagnetic spectrum.

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45- Synthesis, chemiluminescence and energy transfer efficiency of 2,3-dihydrophthalazine-1,4-dione and BODIPY dyad

