DESIGN AND SYNTHESIS OF TRUXENE BASED SOLUTION PROCESSABLE BLUE EMITTING MATERIALS FOR ORGANIC ELECTRONICS

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by

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Dedicated to my grandfather

Mr. Chanan Singh

for always being an inspiration

CERTIFICATE

This is to certify that the thesis entitled "**Design and Synthesis of Truxene Based Solution Processable Blue Emitting Materials for Organic Electronics**" being submitted by **Ms. Banpreet Kaur** to the Indian Institute of Technology Delhi, New Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Ms. Banpreet Kaur** has worked under my guidance and supervision and has fulfilled the requirements for the submission of her thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any other degree or diploma.

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(**BANPREET KAUR**)

ABSTRACT

π-Conjugated luminescent materials are of considerable importance due to their applications in the field of optoelectronics including organic light emitting diodes, light emitting electrochemical cells and fluorescent probes. The solid state emission and full-colour displays, require emission from all three primary colours- red, green and blue of equal intensity and stability. However, the blue emitters, due to their inherent wide band gap, are difficult to obtain as large band gap usually results in inefficient charge injection. Although a plethora of fluorescent blue emitting materials have been reported with moieties like pyrene, anthracene, fluorene, indenofluorene etc., they suffer from problems like aggregation, formation of keto defects and poor thermal stability. Additionally, majority of the reported materials do not possess solution-processability leading to utilization of expensive fabrication/deposition techniques, which have been found unsuitable for large surface area applications. Hence, there is a need to design and develop stable, solution-processable fluorescent blue emitting materials. The compelling properties of truxene scaffold provides it a huge potential as a precursor for the development of active materials for blue emitting OLEDs. Truxene or 10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene is a fused trimer of fluorene, which is a widely reported blue emitting material. This polyaromatic C3 symmetric molecule possesses large π-conjugated system with multiple reactive sites along with high thermal stability, having T_d > 300 °C. Another distinct feature of truxene is its high photoluminescence quantum yield due to its rigid structure. The positions 5,5',10,10',15,15'- can be utilized for introduction of alkyl groups, thereby rendering it soluble in common organic solvents. Apart from that, the positions 2,7,12- are also available for substitution or coupling with other moieties to extend the π-conjugation. Therefore, this research focuses on development of solution-processable truxene based blue emitters exploring various synthetic routes, catalytic and non-catalytic. Additionally, a series of truxene based conjugated polymeric materials has also been developed for blue emission.

In the first section, truxene core has been utilized to synthesize target molecules (**T_1-T_4**) through palladium catalysed Suzuki and Buchwald-Hartwig cross coupling reactions. The solution processability of the materials was improved by introduction of long n-hexyl chains. The photophysical studies of the materials revealed their blue emitting nature, in both solution and solid state. The highest photoluminescence quantum yield was observed in the case of **T_2** corresponding to a value of 0.97. The compounds **T_2** and **T_3** were used as active materials for the fabrication of solution processed, single layer OLEDs, with low turn-on voltage (2-3.3 V) and CIE coordinates corresponding to (0.16, 0.23) and (0.17, 0.36) for **T_2** and **T_3**, respectively. Additionally, a novel extended core of truxene was developed, possessing planar and rigid structure similar to the truxene core. The derivatives prepared from the core, especially target molecule **T_5** were found to have much narrow blue emissions in both solution and solid-state, due to bulkiness of the core preventing the aggregation.

In the next section, modified Debus-Radziszewski reaction was used to design and synthesize series of truxene derived novel blue-emitting materials bearing phenanthroimidazole (**T_6-T_9**) and diphenylimidazole (**T_{10}-T_{13}**) moieties. The facile conditions of the reaction provides a potential for scale-up as well. The materials were prepared by varying the phenyl group attached at the C2 position of phenanthroimidazole and diphenylimidazole moieties. These substitutions were found to have significant effect on the photophysical and electrochemical properties, with molecules bearing cyano substituent **T_8** and **T_{12}** having charge transfer character dominant in their excited state. Also, the materials exhibited good photoluminescence quantum yields as high as 0.83. The optimized geometries obtained from the computational studies revealed the highly twisted

geometries of the molecules, with dihedral angles of up to ~78°. The TCSPC studies of these blue emitters revealed radiative pathways as dominant for deactivation of the excited states.

In the final section, truxene based novel monomers were prepared through common synthetic route. The synthesized monomers were utilized for the design of linear truxene-functionalized homo- and co-polymers through well-established polymerization routes. The homopolymers $\mathbf{P_1}$ and $\mathbf{P_2}$, were prepared through Yamamoto polymerization along with a series of alternating copolymers $\mathbf{P_3}$-$\mathbf{P_8}$, which were prepared by incorporating fluorene and N-carbazole based derivatives as co-monomers, through Suzuki polymerization reaction. The steady-state photophysical studies revealed the deep blue/blue emitting nature of the synthesized polymers. GPC analysis showed a weight-average molecular weight, M_w of up to 57.4 X 10^3 g mol^{-1}. Additionally, the polymers were also found to possess high thermal stability with degradation temperatures up to 400 °C, fulfilling the essential prerequisites as potential blue emitting materials.

सार

π-संयुग्मित लूमिनेसेंट पदार्थ ऑप्टोइलेक्ट्रॉनिक के क्षेत्र- कार्बनिक प्रकाश उत्सर्जक डायोड, प्रकाश उत्सर्जक विद्युत रासायनिक सेल और फ्लोरोसेंट अनुवेदक आदि में अपने अनुप्रयोगों के कारण काफी महत्व रखते हैं। ठोस पदार्थ अवस्था उत्सर्जन और पूर्ण-रंग प्रदर्शन के लिये तीन प्राथमिक रंगों- लाल, हरे और नीले से समान तीव्रता और स्थिरता के उत्सर्जन की आवश्यकता होती है। परन्तु, नीले उत्सर्जक, उनके अंतर्निहित बड़े बैंड गैप के कारण, प्राप्त करना मुश्किल होता है, क्योंकि बड़े बैंड गैप के परिणामस्वरूप आमतौर पर अक्षम चार्ज इंजेक्शन होता है। हालांकि, फ्लोरोसेंट नीले उत्सर्जक पदार्थों का अधिकतम वर्णन मौजूद है, जिसमें पाइरिन, एन्थ्रेसीन, फ्लोरीन, इंडेनोफ्लोरिन आदि जैसे भाग है, वे एकत्रीकरण, कीटो दोष के गठन और खराब थर्मल स्थिरता जैसी समस्याओं से पीड़ित हैं। इसके अतिरिक्त, अधिकांश विवरण किये गए पदार्थों में विलयन-प्रक्रियात्मकता नहीं होती, जो महंगे निर्माण / निक्षेपण तकनीकों के उपयोग की ओर ले जाती हैं, और बड़े सतह क्षेत्र के अनुप्रयोगों के लिए अनुपयुक्त हैं। इसलिए, स्थिर, विलयन-प्रक्रिया योग्य फ्लोरोसेंट नीले उत्सर्जन पदार्थ को डिजाइन और विकसित करने की आवश्यकता है। ट्रुक्सीन स्कैफोल्ड के अप्रतिरोध्य गुण नीले उत्सर्जक ओ. एल. ई. डी. के लिए सक्रिय पदार्थों के विकास में अग्रदूत के रूप में एक बड़ी क्षमता प्रदान करते हैं। ट्रुक्सीन या १०, १५-डाइहाइड्रो - ५ एच - डाइएंडएनो [१, २- एः १', २ '-सी] फ्लोरीन, फ्लोरीन का संगलित त्रितयणु है, जो व्यापक रूप से प्रतिवेदित नीला उत्सर्जक पदार्थ है। इस पॉलयआरोमटिक, सी-३ सममित अणु में विपुल π -संयुग्मित व्यवस्था होती है जिसमें उच्च ताप स्थिरता (T_d > ३०० °C) के साथ कई प्रतिक्रियाशील स्थान होते हैं। ट्रुक्सीन की एक और विशिष्ट विशेषता इसकी अनम्य संरचना के कारण इसकी उच्च फोटोलुमिनसेन्स क्वांटम यील्ड है। ट्रुक्सीन के ५,५ ', १०, १०', १५, १५'-स्थान का उपयोग एल्काइल समूहों को सम्मिलित करने के लिए किया जा सकता है, जिससे यह आम कार्बनिक सॉल्वैंट्स में विलयशील होता है। इसके अलावा, पद २, ७, १२- अन्य उत्सर्जक भागों के प्रतिस्थापन या युग्मन के लिए उपलब्ध हैं जिस से π-संयुग्मन का विस्तार संभव है। इसलिए, यह अनुसंधान विभिन्न संश्लेषण मार्गों, उत्प्रेरक और गैर-उत्प्रेरक, विलयन-प्रक्रिया योग्य ट्रुक्सीन आधारित नीले उत्सर्जकों के विकास पर केंद्रित है। इसके अतिरिक्त, नीले उत्सर्जन के लिए ट्रुक्सीन आधारित संयुग्मित बहुलक पदार्थों की एक श्रृंखला भी विकसित की गई है।

पहले खंड में, त्रुक्सीन कोर का उपयोग लक्ष्य अणुओं (T_1-T_4) को संश्लेषित करने के लिए किया गया है, जो पैलेडियम उत्प्रेरित सुज़ुकी और बुकवाल्द -हार्टविग क्रॉस युग्मन प्रतिक्रियाओं के माध्यम से होता है। लंबी एन-हेक्साइल श्रृंखलाओं के निगमन से पदार्थों की विलयन-प्रक्रियात्मकता में सुधार पाया गया। पदार्थों के फोटोफिजिकल अध्ययन ने उनकी नीली उत्सर्जक प्रकृति को द्रव और ठोस अवस्था दोनों में प्रकट किया। ०.९७ के परिमाण के अनुरूप T_2 के मामले में सबसे अधिक फोटोलुमिनसेन्स क्वांटम यील्ड देखी गई। यौगिक T_2 और T_3 को विलयन संसाधित, इकहरा परत ओ. एल. ई. डी. के निर्माण के लिए सक्रिय पदार्थों के रूप में इस्तेमाल किया गया जिसमे कमतर टर्न-ऑन वोल्टेज (२-३.३ V) और सी. आए. ई. निर्देशांक (०.१६, ०.२३) T_2 के लिए और (०.१७, ०.३६) T_3 पाए गये। इसके अतिरिक्त, त्रुक्सीन के एक नव विस्तारित कोर को विकसित किया गया, जिसमें त्रुक्सीन कोर के समान समतल और अनम्य संरचना पाई गयी। कोर से तैयार किए गए यौगिक, विशेष रूप से लक्ष्य अणु T_5 को विलयन और ठोस-अवस्था दोनों में बहुत संकीर्ण नीले उत्सर्जन देते पाया गया, क्योंकि कोर की स्थूलता एकत्रीकरण को रोकती है।

अगले भाग में, संशोधित डेब्यू-रेडज़िस्यूवेस्की प्रतिक्रिया का उपयोग फेनेंथ्रोइमिडाज़ोल (T_6- T_9) और दयेफेनिलिमिडाज़ोल (T_{10}- T_{13}) भागो संग त्रुक्सीन व्युत्पन्न नव नीले उत्सर्जक पदार्थों की श्रृंखला को डिज़ाइन और संश्लेषित किया गया। प्रतिक्रिया की सुगम परिस्थितियाँ उचित अनुपात में बड़ावे के लिए भी एक क्षमता प्रदान करती हैं। लक्ष्य अणुओं में फेनेंथ्रोइमिडाज़ोल और दयेफेनिलिमिडाज़ोल की सी-२ स्थिति से संलग्न विभिन्न फीनाइल समूह उपयोग किए गये। इन प्रतिस्थापनों का फोटोफिजिकल और इलेक्ट्रोकेमिकल गुणों पर महत्वपूर्ण प्रभाव पाया गया, साईनो (-CN) समूह के साथ अणुओं T_8 और T_{12} की उत्तेजित अवस्था में चार्ज़ स्थानांतरण चरित्र प्रमुख पाया गया। इसके अलावा, पदार्थों ने ०.८३ तक उच्च फोटोलुमिनसेन्स क्वांटम यील्ड का प्रदर्शन किया। कम्प्यूटेशनल अध्ययनों से प्राप्त अणुओं की अनुकूलित ज्यामितीय से अत्यधिक मुड़ ज्यामिति का पता चलता है, जिसमें ~ ७८ ° तक के विकर्ण कोण हैं। इन नीले उत्सर्जकों के टी. सी. एस. पी. सी. अध्ययनों ने उत्साहित अवस्था के निष्क्रियकरण होने के लिए विकिरण मार्ग का प्रभावी योगदान बताया।

अंतिम खंड में, त्रुक्सीन आधारित नव मोनोमर्स सामान्य संश्लेषिक मार्ग के माध्यम से तैयार किए गए थे। संश्लेषित मोनोमर्स का उपयोग त्रुक्सीन-आधारित रैखिक सम- और सह-बहुलको के डिजाइन के लिए स्थापित पोलीमराइज़ेशन मार्गों के माध्यम से किया गया था। सम-बहुलक P_1 और P_2 को यमामोटो पोलीमराइजेशन के साथ

तथा वैकल्पिक सह-बहुलको **P_3-P_8** की एक श्रृंखला जिनको सुजुकी पोलीमराइज़ेशन प्रतिक्रिया के माध्यम से फ्लोरीन और एन-कार्बाज़ोल आधारित डेरिवेटिव को सह-मोनोमर्स के रूप में शामिल करके तैयार किया गया। स्थिर-अवस्था फोटोफिजिकल अध्ययनों ने संश्लेषित बहुलको की गहरी नीली / नीली उत्सर्जक प्रकृति का पता लगाया। जी. पी. सी. विश्लेषण ने वजन-औसत आणविक भार, M_w को ५७.४ x १०^{३} ग्राम मोल$^{-१}$ तक दिखाया। इसके अतिरिक्त, बहुलक को ४०० °C तक उच्च तापीय स्थिरता के लिए भी पाया गया था, जो संभावित नीले उत्सर्जन पदार्थों के रूप में आवश्यक पूर्वापेक्षाओं को पूरा करता है।

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LIST OF ABBREVIATIONS

CIE	Commission Internationale de l'éclairage
CT	Charge Transfer
D-A	Donor-Acceptor
DCM	Dichloromethane
DFT	Density Functional Theory
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DPI	Diphenylimidazole
E_g^{opt}	Optical Band Gap
EQCM	Electrochemical Quartz Crystal Microbalance
EQE	External Quantum Efficiency
ESI	Electrospray Ionization
ETL	Electron Transporting Layer
ETM	Electron Transporting Material
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transporting Layer
HTM	Hole Transporting Material
IQE	Internal Quantum Efficiency
ITO	Indium Tin Oxide
LEC	Light-Emitting Electrochemical Cell
LUMO	Lowest Unoccupied Molecular Orbital
MALDI	Matrix Assisted Laser Desorption/Ionization

NBS	N-bromosuccinimide
n-BuLi	Normal-butyl lithium
NMR	Nuclear Magnetic Resonance
OFET	Organic Field Effect Transistor
OLED	Organic Light Emitting Diode
OPV	Organic photovoltaics
PAH	Polyaromatic Hydrocarbons
PEDOT-PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PIM	Phenanthroimidazole
PLED	Polymer Light Emitting Diode
PLQY	Photoluminescence Quantum Yield
PPV	Poly(p-phenylene vinylene)
PSC	Polymer Solar Cell
RISC	Reverse Inter-System Crossing
SMOLED	Small Molecule Organic Light Emitting Diode
TADF	Thermally Activated Delayed Fluorescence
TBAB	Tetra-n-butylammonium bromide
TCSPC	Time-Correlated Single Photon Counting
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TPBI	1,3,5-tri(phenyl-2-benzimi-dazolyl)-benzene

LIST OF CHEMICAL FORMULAE

KOH	Potassium Hydroxide
H_2SO_4	Sulphuric acid
HNO_3	Nitric Acid
HCl	Hydrochloric acid
$Pd(dppf)Cl_2$	1,1'Bis(diphenylphosphino)ferrocene]dichloropalladium(II)
$FeCl_3$	Ferric Chloride
NaOH	Sodium Hydroxide
$Ni(dppp)Cl_2$	Propane 1,3-bis(dphenylphosphino) Nickel
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
K_2CO_3	Potassium Carbonate
NaH	Sodium Hydride
Na_2SO_4	Sodium Sulphate
KOH	Potassium Hydroxide
KO^tBu	Potassium tert-butoxide
EtOH	Ethanol
Pd_2dba_3	Tris(dibenzylideneacetone)dipalladium(0)
$Ni(COD)_2$	Bis(cyclooctadiene)nickel(0)
COD	1,5-Cyclooctadiene
NH_4Cl	Ammonium Chloride
$SnCl_2.2H_2O$	Tin (II) Chloride Dihydrate
CCl_4	Carbon Tetrachloride
Br_2	Molecular Bromine
$CHCl_3$	Chloroform

KCl	Potassium Chloride
CsF	Cesium Fluoride
LiF	Lithium Fluoride