Synthesis and Characterization of naphthalene and tetraphenyl
benzidine
based electrochromic molecules

By

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Abstract

Synthesis of electrochromic monomers are the primary focus of this dissertation. The overall objectives include: (i) to design naphthalene diimide (NDI)-based chromophores with different electrochromic properties for direct use in electrochromic devices (ECDs) and (ii) to design crosslinkable tetraphenylbenzidine (TPB) based chromophores for simplifying the solution process in ECDs fabrication.

The synthesis of NDI based chromophores including **DPy-N4-NDI**, **DPy-N3-NDI** and **DPy-N2-NDI** were achieved by direct imidization using 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and appropriate choice of amino pyridines. Pyridine modified NDIs are further reacted with 1-iodomethane and 6-bromohexane to form **DM-N2-NDI2I**, **DM-N3-NDI2I**, **DM-N4-NDI2I**, **DH-N3-NDI2Br** and **DH-N4-NDI2Br**. All chromophores are electroactive, and the electrochromic features are governed by structural factors. Due to the same naphthalene core, all chromophores exhibit reversible color change from pale yellow, to brown, then dark green with different operational voltage ranging from -12mV to -134 mV for the first reduction and -334 mV to -598 mV for the second reduction.

The synthesis of TPB based cross linkable chromophores are achieved through Buchwald-Hartwig coupling reaction. Indole was introduced to tetraphenylbenzidine (TPB) as the cross-linkable group for solution processible TPB. The branched indole TPB and fused indole TPB are successfully obtained and proved by corresponding proton NMR spectrum.

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List of abbreviations and symbols

CE	coloration efficiency
DMF	dimethylformamide
DMSO	Dimethyl sulfoxide
ECD	electrochromic devices
E_g	Energy gap
ES	Everitt's salt
HOMO	highest occupied molecular orbital
IR	infrared
IVCT	intervalence charge transfer
LLCT	ligand-to-ligand charge transfer
LUMO	lowest unoccupied molecular orbital
MLCT	metal-to-ligand charge transfer
MMA	methyl methacrylate
MV	1,1'-di-methyl-4,4'-bipyridilium
NDTA	1,4,5,8-naphthalenetetracarboxylic dianhydride
NIR	near infrared
OFET	organic field effect transistor
OLED	organic light emitting diode
PANI	polyaniline
PEDOT	Poly[3,4-(ethylenedioxy)thiophene]
PG	Prussian green
PPy	polypyrrole

PSC	perovskite solar cell
PSS	polystyrene sulfonate
PT	polythiophene
PY	Prussian yellow
TCNQ	tetracyanoquinodimethane
TPA	triphenylamine
TTF	tetrathiofulvalene
UV	ultraviolet
VBV	vinylbenzyl viologen
vis	visible

Chapter 1. Introduction to electrochromic materials

Chapter 1. Introduction to electrochromic materials

This chapter provides background information on various types of electrochromic materials.

1.1. Electrochromic materials

Chromic materials, which represent a class of materials which can change colors or light absorptions with external stimulus, attracted considerable interests due to the wide applications in information displays, smart windows, variable reflectance mirrors, bio-imaging, thermal control and camouflage materials. Basing on the types of materials, chromic materials can be classified into inorganic, organic chromic materials. Basing on the external stimulus, they can be divided into electrochromic (voltage), photochromic (light), mechanochromic (mechanical forces), solvatochromic (polarity), halochromic (acidity) and thermochromic (temperature) materials *etc.*

Electrochromic materials refer to a class of material can undergo reversible color or light absorption change with the application of an external electric field.¹ The history of electrochromic materials can be dated back to 1961 when the concept of electrochromism phenomena was firstly proposed by John R. Platt.² In 1969, Del et al. demonstrated the electrochromic behavior of the amorphous metal oxides film at Cyanamid Corp which is widely recognized as the true birth of the electrochromic technology.³ After 1980s, the studies of electrochromic material were mainly focused on the commercialization of electrochromic materials.⁴ C.G. Granqvist reported the

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construction of smart windows by applying WO_3 on the surface of transparent conductor which is the commence of the commercial application of electrochromic materials.⁵

Figure 1. 1. Commercial applications of electrochromic material: a) auto-dimming rear mirror; b) electric area plane window; c) e-paper; d) display; e) electrochromic laminated glass¹⁻⁶

As shown in Figure 1.1, smart windows for use in aircrafts, anti-glare car rear mirrors, electric papers and electric displays are the main commercial application of the electrochromic materials. In the designing of candidates for electrochromic devices (ECD), several parameters needed to be considered including color efficiency, electrochromic contrast ratio, switching speed and electrochemical stability.^{1,6,7} The typical structure of commercially available electrochromic devices (ECD) is mainly

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consisted of electrochromic materials as the working layer, transparent electrodes, electrolytes and insulating substrates as shown in Figure 1.2.

Figure 1. 2. Schematic representation of electrochromic devices (ECD) structure⁸

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1.2. Different types of electrochromic materials

In general, there are two different categories of electrochromic materials in terms of the chemical composition including inorganic and organic electrochromic materials. Typical inorganic electrochromic material includes transition metal oxides and Prussian blue.⁸⁻¹⁰ Organic electrochromic can be classified as small molecular dyes and conjugated polymers.¹¹

1.2.1. Inorganic electrochromic materials

Transition metal oxides including tungsten, nickel, iridium and molybdenum show the most intensive electrochromic behavior. Among these transition metal oxides, tungsten trioxide (WO_3) and nickel oxide (NiO) have been widely investigated and utilized over the last 40 years due to the long-term chemical and cyclic stability, good initial transparency and high coloration efficiency.^{12,13}

1.2.1.1. Transition metal oxides

WO_3 is known as the mostly popular cathodic electrochromic material which changes color from transparent to dark blue under reductive potential. Tungsten performed a reversible color change between oxidation state (W^{VI}) showing transparent or pale yellow color, and tungsten bronze (W^{V}) which is generated through double injection of protons and electrons giving a deep blue color.^{14,15} It shows different colors reacting to different voltages, as shown in Figure 1.3.. This electrochromic color change can be expressed as following in which M stands for the cations (Li, H, Na) in the electrolytes:

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The coloration efficiency (CE) of WO_3 is strongly depending on the level of crystallization for the reason that the color change reaction is relying on the diffusion of cation.^{15,16} Amorphous WO_3 ECDs received most of the investigations so far because of good coloration efficiency and fast switching speed.¹⁷ But the cyclic and electrochromic stability is poor which limited the long term application. Crystalline WO_3 has a denser form resulting in a better stability.¹⁸ However, comparing to the amorphous analogous, crystalline bulk WO_3 has a lower coloration efficiency and slow switching speed due to the dense structure.

Figure 1. 3. Color change of WO_3 film at different potentials¹⁹

The methods for preparing WO_3 thin film includes vapor-phase syntheses and liquid-phase syntheses. Vapor-phase syntheses refers to the deposition of vaporized electrochromic materials on the transparent surface of electrode.²⁰ The techniques widely reported contains sputtering coating, thermal evaporation, electron-beam deposition and pulse-laser deposition. Liquid-phase syntheses is an alternative method for processing films with a lower cost, for instance, sol-gel technique.^{15,21}

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NiO performs a reversible color change between transparent (neutral state) and dark brown (oxidized state). The color change reaction can be written as follows:

ECDs basing on NiO film have been fabricated using multiple methods including sputtering and sol-gel method.^{22,23} NiO ECDs commonly show a high electrochromic efficiency, great optical transmittance changes, good reversibility and have relatively low material cost. But NiO system in liquid electrolyte suffers from poor durability. Gel state lithium electrolyte based nickel oxides, which is considered as the alternative structure due to the better stability, performed small optical changes.²⁴

Other transition metal oxides including molybdenum, vanadium, iridium and titanium are also electrochromic. Their coloration and bleached states are concluded as follows:

Table 1. 1. Transition metals and their color changes

Electrochromic transition metals	Coloration states	Bleached states
V ₂ O ₅	Brown-yellow	Very pale blue
MoO ₃	Deep blue	Colorless
IrO ₂	Blue-black	Colorless
TiO ₂	Blue-green	Colorless

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1.2.1.2. Prussian Blue

Another category of inorganic electrochromic materials is Prussian blue (PB), which is famous for the good durability, quick response time and multi-color electrochromic behavior.²⁵⁻²⁷ Prussian blue is blue in neutral state and it can be reduced to Everitt's salt (ES) which is colorless. It also can be partially oxidized to Prussian green (PG) and completely oxidized state which gives a Prussian yellow color (PY). The color change reaction can be presented as follows:

PB ES (colorless) (Reduced)

PB PG (green) (Partially oxidized)

PB PY (yellow) (complete Oxidized)

After the first ECD based on Prussian blue reported by T. Miyamoto *et al* in 1987, PB is commonly used as information displays, batteries and electroanalytic sensors.²⁸⁻³¹

Inorganic electrochromic materials have many advantages including long cyclic life, good durability, high colored/bleached contrast, memory effect and energy

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saving. However, the application has been limited by the disadvantages they possess, including high material and processing cost, toxicity and slow switching speed.

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1.2.2. Organic electrochromic materials

In general, there exists two main categories of organic electrochromic materials, including small organic dyes and conjugated polymers. Compared to the inorganic analog, typical advantages of organic electrochromic materials include low material cost, short response time, low operation potential, various colors display.^{11,32}

1.2.2.1. Small molecular electrochromic materials

Small molecular electrochromic materials includes viologen derivatives,^{33–35} tetrathiofulvalene (TTF) derivatives,³⁶ tetracyanoquinodimethane (TCNQ) derivatives³⁷ and transition metal complex^{38,39}.

(1) Viologens

1,1'-Disubstituted-4,4'-bipyridinium salts, also known as 'viologen', are commonly used as herbicides, antibacterial agent and redox indicator.³⁴ The prototype of viologen, which is 1,1'-di-methyl-4,4'-bipyridinium (MV), has three redox states, namely, neutral, radical cation and di-cation. MV is colorless in di-cation state and it can be reduced to radical cation exhibiting a dark blue color, then natural state as shown in Scheme 1.1. The di-reduces MV shows very low color intensity due to the reason that there is no charge transfer or internal transition corresponding to the visible wavelength. Other viologens with replaced R groups are named as substituent viologens which can exhibit different color changes.

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Scheme 1. 1. The reversible change between three redox state of viologen

The synthetic procedures of MV or substituent viologens are usually carried out in polar aprotic solvents such as acetonitrile (CH_3CN), dimethylformamide (DMF), with excessive alkylating reagents and 4,4'-bipyridine. Asymmetric alkylation can be achieved by tuning the ratio between bipyridine and alkylating reagent. Crosslinked viologen based polymer was reported by Kao *et al.* in 2016.³⁵ They synthesized vinylbenzyl viologen (VBV), then polymerized it with methyl methacrylate (MMA) to give a polymeric viologen based electrochromic material, as shown in Figure 1.4.

Figure 1. 4. Synthesis of VBV and MMA copolymer³⁵

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Viologen based ECDS has been long commercialized since the C.J. Schoot *et al.* reported the first viologen based electrochromic memory display in Holland in 1973.⁴⁰ The ready availability of 4,4'-dipyridine and the ease of the structural tuning allows intensive researches driving into the electrochromic behavior of viologens. However, viologen based devices are also facing some drawbacks, for instance, stability.

(2) Transition metal complexes

Another class of small molecular organic dyes are transition metal complex including iridium, platinum, ruthenium, rhenium and tungsten. Ligands are commonly nitrogen, oxygen or sulfur containing organic small molecules. Transition metal complexes exhibit color changes through isomerization which is usually induced by metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT) or intervalence charge transfer (IVCT).^{41,42}

Among these transition metals, ruthenium (II) complexes are thought to be the most promising and versatile candidate for electrochromic materials.^{43,44} In 2016, Lisheng Zhang *et al.* studied the relationship between color change and ligand modification based on $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ as shown in Figure 1.5. They found the stability of $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ isomers are increased by the electron withdrawing group on sulfur. Also, electron withdrawing group will increase the absorption energies of $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ isomers, thus change the electrochromic properties.

Figure 1. 5. Chemical structure of ruthenium sulfoxide reported by Lisheng Zhang et al⁴⁴

1.2.2.2. Conjugated conducting polymers

The class of conjugated conducting polymers used in ECDs are normally consisting of homopolymers⁴⁵ and copolymers⁴⁶. Conducting polymers undergoes an oxidation upon an external positive voltage to give a color, which means the materials are populated with positive charged centers and possess a delocalized π -electron band structure, are generally termed as “p-doping” or “anodically coloring”. Conversely, if a polymer gives a color under an external negative voltage, it can be termed as “n-doping” or “cathodically coloring”. The terminology described which electrode the material will contact when the electrochromic reaction undergoes. Optical properties are determined by the intrinsic optical bandgap (E_g) which is the bandgap magnitude

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between the highest-occupied π -electron band (the valence band) and the lowest-unoccupied π -electron band (the conduction band). In conducting polymer based ECDs, the polymers are processed into thin films on transparent electrodes through spin coating, dip coating or direct electropolymerization.

(1) Homopolymer

Among all homopolymers, polythiophene (PT), polyaniline (PANI) and polypyrrole (PPy) are of particular interests due to their structural tunability, good processability, electrochemical stability and ease of synthesis.

A large number of substituted 3-substituted thiophene and 3,4-disubstituted thiophene for polymerization have been synthesized and commercialized due to the poor solubility and processability of polythiophene.⁴⁷ The parent polythiophene has a red color ($\lambda_{\text{max}} = 470 \text{ nm}$) in undoped form and a blue color ($\lambda_{\text{max}} = 730 \text{ nm}$) in the doped form. The electrochemical and optical properties can be altered through the side group modification. For example, poly(3-methylthiophene) is purple in neutral state and turns into pale blue upon oxidation as shown in Figure 1.7.⁴⁸ Colors available of polythiophene derivatives, which is ascribed to the effective conjugation length of the polymer backbones, includes pale blue, blue and violet in the oxidised form, and purple, yellow, red and orange in the reduced form.¹¹

Figure 1. 6. Polythiophene based ECDs under operation⁴⁸

Polythiophene derivatives have been intensively investigated due to higher contrast ratio, faster switching speed and good processability through increased solubility. J. R. Reynolds *et al.* studied the electrochromic properties of a series of thiophene containing polymer for ECDs recently as show in Figure 1.8.^{49–52} Compared to other alky-substituted polythiophenes, Poly[3,4-(ethylenedioxy)thiophene] (PEDOT) based ECDs have a lower bandgap, better stability and high electric conductivity. The band gap of PEDOT ($E_g = 1.6$ eV) is 0.5 eV lower than polythiophene, which is owing to the two electron donating oxygen atoms. In 1988, PEDOT was synthesized and patented by a group of scientists in Bayer AG research laboratories in Germany in attempt to develop a new easy oxidized and stable polythiophene drivative.⁵³ The solubility of PEDOT is enhanced by adding a water-soluble polymer, polystyrene sulfonate (PSS), which allows various applications of PEDOT for electrical devices including ECDs, solar cells, ink etc.

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Figure 1. 7. Polythiophene derivatives library

Polyaniline (PANI) thin films exhibit color change from transparent yellow to green, then dark blue and black, upon external oxidative voltage.⁵⁴ As shown in Figure 1.9, PANI undergoes a two-step oxidation reaction, giving a green color at -0.2 V and a dark blue color at 0.5 V. At 1 V, PANI displays a black color. Stable color change between transparent yellow and green can be achieved with a life cycle higher than 10^6 times.⁵⁵ However, after 20 circles, the reversibility of color change between deep blue and black decreases dramatically.

Figure 1. 8. Cyclic Voltammetry of PANI thin film. (—) First scan; (---) after 20 cycles; (-.-) after 300 cycles.⁵⁵

Numerous substituted polyanilines have been synthesized and utilized as electrochromic material. In 1995, R.J. Mortimer reported the electropolymerization of 2-methylaniline and 3-methylaniline in attempt to increase the electrochemical stability with similar optical properties of polyaniline, as shown in Figure. 1.10.⁵⁶

Figure 1. 9. Cyclic voltammetry of Poly(2-methylaniline) (Left) and poly(3-methylaniline) (Right); Optical properties comparison with polyaniline⁵⁶

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Combining PANI and transition metal oxides is another strategy in fabricating complementary ECDs. G. Cai *et al.* reported the incorporation of TiO₂ and polyaniline to obtain enhanced performance electrochromic films.⁵⁷ The TiO₂ nanorod arrays are prepared on fluorine doped tin oxide (FTO) glass through a hydrothermal process. Then PANI was coated on the surface of the nanorods through electropolymerization to give a core/shell structure. The hybridization of PANI and TiO₂ nanorods arrays provide a reversible color change between pale yellow and dark purple with good stability.

Figure 1. 10. a) Schematic of the formation of PANI coated TiO₂ nanorods arrays; b) Reversible color change; c) SEM image of TiO₂/PANI cooperated film; d) Cyclic voltammetry comparison between TiO₂, PANI and TiO₂/PANI cooperated film⁵⁷

(2) Copolymers

Copolymer electrochromic devices can be obtained through electropolymerization or chemical polymerization of two or more electroactive chromophores possessing different optical properties than their parent homopolymers.

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Tuning the ratios between the different chromophores provide a large family of multicolored polymer materials. L. Toppare reported the electropolymerization of 1-(Phenyl)-2,5-di(2-thienyl)-1H-pyrrole (PTP) and 3,4-ethylenedioxy thiophene (EDOT) with 1:1 ratio as shown in Figure 1.12.⁵⁸ Consecutively, the electrochromic properties of the copolymer (P(PTP-co-EDOT)) was compared with PDEOT. The conductivity of P(PTP-co-EDOT) was found to be higher than PPTP caused by the introduction of EDOT moiety, which increase the effective conjugation length. Band gap of P(PTP-co-EDOT) is 1.9 eV which is lower than PEDOT.

Scheme 1. 2. Synthesis of P(PTP-co-EDOT)⁵⁸

Chromophores can be divided into 2 categories, namely, donor (electron rich monomers) and acceptor (electron deficient monomers). Donor, herein, is referred as the electron donating group which will decide the highest occupied molecular orbital (HOMO) and acceptor is referred as the electron accepting group which can decide the lowest unoccupied molecular orbital (LUMO). By appropriate choosing and integration of donors and acceptors in one polymer, band gap can be finely controlled to adjust the optical properties of the copolymers.^{59,60} Donor-Acceptor polymers (d-A

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polymers), which has an alternating array of donor and acceptor, has been proved too be very effective for tailoring the band gap.

Thiophene and thiophene derivatives are donors of significant importance. The modification of thiophene focused on the side chain alkylation for increasing solubility, side chain arylation for extending conjugation and ring fusion.^{47,61} Another important donor group is triphenyl amine (TPA). TPA based electrochromic materials present good coloration efficiency, good contrast ratio and low operation potential.⁶² In 2013, C. Zhang group reported the synthesis of poly(4,4',4''-tris[4-(2-bithienyl)phenyl]amine) (PTBTPA).⁶³ They incorporated triphenyl amine as the core and thiophene as the cross-linkable group together. PTBTPA presented enhanced stability, redox reversibility and better contrast ratio compared to its parent polymers.

Commonly used donors and acceptors are listed in Figure 1.13.

Figure 1. 11. Commonly used donors and acceptor for D-A polymers

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1.3. Applications of Electrochromic material

As previously mentioned, electrochromic materials have been long used as information displays, smart windows and antiglare mirrors. To date, a large number of novel applications of electrochromic materials have been developed. As shown in Figure 1.12, Stephen H. Foulger *et al.* incorporated PANI and PEDOT with silica colloidal as ink in 2008.⁶⁴ PANI-silica and PEDOT silica composites have a diameter between 200 to 300 nm which can be directly inkjet-printed by commercial available printer. Inkjet printing electrochromic device enables ECDs fabrication with even lower cost.

Figure 1. 12. Schematic of inkjet-printable PANI-silica and PEDOT silica composites⁶⁴

Another interesting application of electrochromic materials is light-pen input device reported by Isao Shimoyama group in 2008.⁶⁵ Touchpad is the most common input device, which is consisting of two transparent electrode separated by air gap. BacterialRhodopsin (bR), a photo sensitive protein, is easy to process into film and compatible with large area flexible display. They demonstrate a touch pad with

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PEDOT: PSS as the working electrodes, making device flexible and bR, which is working as the photosensors.

Figure 1. 13. Schematic of inkjet-printable PANI-silica and PEDOT silica composites⁶⁵

1.4. Rationale and objectives

Organic electrochromic materials are of distinguished features mainly depended on the magnitude of band gap, which gives particular optical and electrical properties to electrochromic devices. In addition to the electrochromic properties, solubility and film processability are the main purposes of this research.

In this first part, the research is interested in development and study of naphthalene based electrochromic dyes with good solubility. Also, polymers of naphthalene diimides will be attempted.

The second part will focus on the synthesis of cross-linkable triphenyl amine chromophores.

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1.4.1. Synthesis of naphthalene based electrochromic small molecules

To synthesise the five naphthalene diimides based chromophores, having different conjugation length. The electrochromic properties will be studied using optical transparent thin layer electrochemical cell.

1.4.2. Synthesis of cross-linkable triphenylene amine based electrochromic molecules

To synthesise two triphenyl amine-based chromophores with cross-linkable group through Buchwald-Hartwig coupling reaction.

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1.5. References

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Chapter 2. Electrochromic naphthalene diimides compounds

2.1. Introduction

Typical organic electrochromic materials are normally p-doping materials, both in the class of small molecules and polymers. Among aromatic molecules that have been used in ECDs, 1,4,5,8-naphthalene diimides (NDIs) have attracted much attention because of their tendency to form n-doping electrochromic materials.¹ NDIs, a type of compact, electron deficient aromatic compound, possess features including high electron affinity, excellent charge carrier mobility and good chemical and thermal stability. It has been reported to undergo two reversible one-electron reductions: $E_{1/2}^{\text{Red1}} = -1.10$ V and $E_{1/2}^{\text{Red2}} = -1.51$, versus ferrocene/ferrocenium (Fc/Fc^+) (LUMO energy = -3.7 eV) as show in Figure 2.1. NDIs present green color upon the first reduction and dark brown color upon the second reduction.^{2,3} NDIs are finding use in organic electronic devices, supramolecular self-assembled architecture, and donor-acceptor system.⁴

Scheme 2. 1. Two one-electron reductions of naphthalene diimides

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NDIs are synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDTA) through a clean one-step imidization with appropriate primary amine in a high boiling porin solvent, such as dimethylformamide (DMF). Reaction time is highly depending on the nucleophilic nature of the amines and reaction temperature. Potassium hydroxide (KOH) is used as the driven force for low temperature reactions (<60 °C), when low boiling point amines are used. By carefully control the pH of reaction mixture, Asymmetric naphthalene diimides can be obtained through a two-step reaction with different target amines.⁵ The product can be collected by filtration after reaction system cooled down and purified by washing with hot DMF.⁶ In 2006, J. K. M. Sanders group reported micro-wave assisted synthesis of symmetric and asymmetric NDIs, as shown in Scheme 2.1.⁷ With the assistance of the micro-wave, the reaction can quantitatively proceed within 5 mins.

Scheme 2. 2. Micro-wave assisted symmetric and asymmetric NDIs synthesis⁷

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Because of the planar aromatic structure, NDIs usually exhibit rather poor solubility in organic solvents used in fabricating electronic device, such as chloroform. NDIs with long aliphatic substituent on imide nitrogen atoms generally have higher solubility.⁸ But the optical and electrochemical properties of NDIs are not tunable due to the lack of π -conjugation extension.

Herein, a series amino pyridines modified NDIs (**DPy-N4-NDI**, **DPy-N3-NDI** and **DPy-N2-NDI**) were synthesized through a clean one-step reaction with quantitative yields.⁹ Pyridinium salts was obtained though the reaction between each pyridine group and corresponding alkyl halides (1-iodomethane and 1-bromohexane) followed by the method developed by Dr. Xiansheng Meng. Electrochemical properties of the resulted products will be characterized using CV and UV using an optical transparent thin layer electrochemical cell (OTTLE cell).

2.2. Results and discussion

2.2.1. Synthesis of small molecules

As shown in scheme 2.1, **DPy-N4-NDI**, **DPy-N3-NDI** and **DPy-N2-NDI** were obtained through direct imidization of 1,4,5,8-naphthalenetetracarboxylic anhydride (NDTA) with different amino pyridines in refluxing DMF with good yields. The reaction mixture slowly dissolved into DMF to form a deep red solution with the temperature increasing and crude product precipitated when imidization reaction is

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finished. Upon cooling to room temperature, product was collected by filtration and washed with DMF for several times.

Scheme 2. 3. Synthesis of naphthalene diimides small molecules

The synthesis of all NDI pyridiniums were achieved by similar manners using excessive iodomethane or 1-bromohexane. Crude product was filtered out and characterized by proton NMR. The ^1H NMR spectrum showed new peaks around 4.7 ppm which indicated the non-aromatic protons on alkyl chain as shown in Figure 2.1.

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Figure 2. 1. NMR of *DH-N4-NDI2Br*

Scheme 2. 4. Synthesis of NDI pyridiniums

2.2.2. IR characterization

IR analysis was conducted using KBr pellet after crude product dried from oven under vacuum. Complete imidization was evident by the vanish of typical C=O

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anhydride peak at 1780 cm⁻¹ and the arise of the imide peak around 1715 and 1672 cm⁻¹ as shown in Figure 2.2.

Figure 2. 2. IR spectrum of DPy-N2-NDI

2.2.3. Electrochemistry

Using an OTTLE cell, the cyclic voltammetry of **DM-N2-NDI2I**, **DM-N3-NDI2I**, **DM-N4-NDI2I**, **DH-N3-NDI2Br** and **DH-N4-NDI2Br** was recorded in DMSO using 0.1 M tert-n-butylammonium perchlorate as the supporting electrolyte. Typical OTTLE cell structure is shown in Figure 2.3. All these chromophores show two reversible one-electron reductions. The first $E_{1/2}$ is subjected to the reduction from neutral state to radical anion, followed by the second reduction subjected to the formation of the dianion.

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Figure 2. 3. Typical structure of an Optical Transparent Thin Layer Electrochemical cell
(<https://www.sigmaaldrich.com/catalog/product/sial/z803758?lang=en®ion=CA>)

CV of **DH-N3-NDI2Br** is depicted in Figure 2.3 (a) to demonstrate the electrochemical activities of typical naphthalene diimides. The first reduction of **DH-N3-NDI2Br** starts at -134 mV giving the material a dark brown color and the second reduction happens at -468 mV showing a green color. The multi-color change is reversible and subjected to the diffusion speed of small molecules in DMSO.

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Figure 2. 4. a) Cyclic voltammetry of DH-N3-NDI2Br; b) color change of DH-N3-NDI2Br in OTTE cell

The first $E_{1/2}$ of **DM-N4-NDI2I** is the lowest which explain the coloration is very quick after the potential was applied during the test. Similarly, the second $E_{1/2}$ of **DM-N2-NDI2I**, which is -309 mV, is much lower than other analogs. The second coloration of **DM-N2-NDI2I** from brown to deep green appear at a lower voltage than other analogs can be attributed to the lower $E_{1/2}$. $E_{1/2}$ data of naphthalene diimides are summarized in Table 2.1.

Table 2. 1. Electrical data for DM-N2-NDI2I to DH-N4NDI2Br

	$E_{a,p} (1)$	$E_{c,p} (1)$	$E_{1/2} (1)$	$E_{a,p} (2)$	$E_{c,p} (2)$	$E_{1/2} (2)$
DM-N2-NDI2I	-24 mV	-24 mV	-24 mV	-334 mV	-284 mV	-309 mV
DM-N3-NDI2I	-24 mV	-42 mV	-33 mV	-438 mV	-428 mV	-433 mV

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DM-N4-NDI2I	-12 mV	-32 mV	-22mV	-396 mV	-431 mV	-414 mV
DH-N3-NDI2Br	-134 mV	-16 mV	-75 mV	-598 mV	-468 mV	-533 mV
DH-N4-NDI2Br	-34 mV	-60 mV	-47 mV	-464 mV	-482 mV	-473 mV

Spectroelectrochemistry measurement were carried out in an OTTLE cell. UV-vis-NIR spectrum was monitored over the complete reduction of all species. Each UV-vis-NIR spectrum was obtained after the specific potential applied for 60 s and maintained throughout the entire measurement. All small molecules are electrochromic as evident by observed spectroelectrochemistry. Upon the reduction of the naphthalene diimides from the neutral state, a red shift from 361 nm, 377nm to 460 nm appears as shown in Figure 2.5 to Figure 2.9. The second reduction, from radical anion state to dianion, include a blue shift from 460 nm to 395 nm, 416 nm except for **DM-N3-NDI2I** as shown in Figure 2.6. The reason could be the voltage for oxidizing **DM-N3-NDI2I** radical cation is higher than its analogues. The higher oxidizing potential can be explained by the stereo-hindrance caused by the 3 position of nitrogen on pyridine ring of **DM-N3-NDI2I**.

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Figure 2. 5. UV-vis-NIR spectroelectrochemistry of DM-N4-NDI2I from neutral state to -900 mV

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Figure 2. 6. UV-vis-NIR spectraelectrochemistry of DM-N3-NDI2I from neutral state to -1500 mV

Figure 2. 7. UV-vis-NIR spectraelectrochemistry of DM-N2-NDI2I from neutral state to -1000 mV

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Figure 2. 8. UV-vis-NIR spectroelectrochemistry of DH-N4-NDI2Br from neutral state to -1000mV

Figure 2. 9. UV-vis-NIR spectroelectrochemistry of DH-N3-NDI2Br from neutral state to -1000mV

2.3. Conclusion

DPy-N4-NDI, **DPy-N3-NDI** and **DPy-N2-NDI** are synthesized through direct imidization with appropriate amino pyridine. All the NDIs exhibit strong absorption at 1780, 1715 and 1672 cm^{-1} indicating the formation of imide on the naphthalene core. In addition, the structure is confirmed by the proton resonances around 7.5 ppm.

The formation of **DM-N2-NDI2I**, **DM-N3-NDI2I**, **DM-N4-NDI2I**, **DH-N3-NDI2Br** and **DH-N4-NDI2Br** are evidenced by the proton resonance at 4.51 ppm indicating the formation of pyridiniums.

All naphthalene-based chromophores display multi-color change from pale yellow, to brown, then dark green with operational voltage ranging from 900 mV to 1500 mV which is lower than that of typical naphthalene imide. Naphthalene based chromophores obtained can be directly used in small molecules electrochromic devices.

2.4. Experimental section

Material

All the materials and reagents were used as received from commercial sources without further purification. Solvent for chemical synthesis were purified by distillation and stored with 4Å molecular sieves. Chemical reactions were carried out under an argon atmosphere.

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Instruments

¹H NMR (300 Hz) spectra were recorded using a Bruker Avance 300 NMR spectrometer. Resonances were quoted on the δ scale relative to tetramethylsilane (TMS, $\delta = 0$) as an internal standard. For ¹H-NMR spectra, the following abbreviations have been used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. FTIR was recorded using a Bio-Rad FTS-135 spectrophotometer. The following abbreviations have been used in IR spectra: s = strong, m = medium, w = weak, br. = broad, sh = sharp. The measuring mode was %T (percentage transmittance). The bands were expressed in cm⁻¹ (per centimeter). Cyclic voltammetry was performed using a BAS 100B/W electrochemical workstation. In-situ spectroelectrochemistry was performed by using an OTTLE (Optically Transparent Thin Layer Electrochemistry) cell consisting of a platinum wire as the working electrode, a platinum wire as the counter electrode and a silver wire as the reference electrode. The UV-vis-NIR spectra was monitored over the complete reduction of the electroactive species. Each UV-vis-NIR spectrum was obtained after holding the specified applied potential for 90s and was maintained over the entire measurement.

Synthesis of small molecules

2,7-di(pyridin-4-yl) benzo[lmn][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (DPy-N4-NDI)

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In a dry 2 neck round bottom flask, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (0.8g, 3mmol) and 4-amino pyridine (0.6g, 6.4mmol) were suspended in anhydrous DMF (20 ml). The mixture was heated at 150 °C for 2hr. A crystalline solid precipitated out, when the reaction was cooled to room temperature. The crude product was collected by filtration and purified by several recrystallization from DMF. The pure compound was obtained as pale-yellow needle-shape crystal (1.08g, 86% of yield). ¹H NMR (300 MHz, DMSO-*d*₆) 8.81(d, 4H), 7.98(d, 4H), 7.60(d, 4H)

2,7-di(pyridin-3-yl) benzo[lmn][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (DPy-N3-NDI)

In a dry 2 neck round bottom flask, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (0.8g, 3mmol) and 3-amino pyridine (0.6g, 6.4mmol) were suspended in anhydrous DMF (20 ml). The mixture was heated at 150 °C for 2hr. A crystalline solid precipitated out, when the reaction was cooled to room temperature. The crude product was collected by filtration and purified by several recrystallization from

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DMF. The pure compound was obtained as pale-yellow powder (844mg, yield of 67%). ¹H NMR (300 MHz, DMSO-*d*₆) 8.72 (d, 4H), 8.09 (d, 2H), 7.65 (t, 2H), 7.51 (d, 2H), 7.31 (t, 2H)

2,7-di(pyridin-2-yl) benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (DPy-N2-NDI)

In a dry 2 neck round bottom flask, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (0.8g, 3mmol) and 2-amino pyridine (0.6g, 6.4mmol) were suspended in anhydrous DMF (20 ml). The mixture was heated at 150 °C for 2hr. A crystalline solid precipitated out, when the reaction was cooled to room temperature. The crude product was collected by filtration and purified by several recrystallization from DMF. The pure compound was obtained as pale-yellow powder (982mg, yield of 78%). ¹H NMR (300 MHz, DMSO-*d*₆) 8.70 (d, 4H), 8.68(s, 2H), 8.22-8.10 (m, 4H), 7.60(t, 2H)

4,4'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8] phenanthroline-2,7-diyl)bis(1-methylpyridin-1-ium) (DM-N4-NDI2I)

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In a dry 2 neck round bottom flask, **DPy-N4-NDI** (91 mg, 0.18 mmol) was added into DMAc (20 ml), then iodomethane (0.25 g, 1.8 mmol) was added into the solution dropwise. After heating at 90 °C for 24 hr, the reaction was cooled to room temperature and the precipitation was collected by filtration and washed with 20 ml of cold ethyl ether. The pure compound was obtained as a red solid (89 mg, yield of 86%). ¹H NMR (300 MHz, DMSO-*d*₆) 9.25 (d, 4H), 8.83 (d, 4H), 8.35 (d, 4H), 4.47 (s, 6H)

3,3'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn] [3,8] phenanthroline-2,7-diyl)bis(1-methylpyridin-1-ium) (DM-N3-NDI2I)

In a dry 2 neck round bottom flask, **DPy-N3-NDI** (91 mg, 0.18 mmol) was added into DMAc (20 ml), then iodomethane (0.25 g, 1.8 mmol) was added into the solution dropwise. After heating at 90 °C for 24 hr, the reaction was cooled to room temperature and the precipitation was collected by filtration and washed with 20 ml of cold ethyl ether. The pure compound was obtained as a deep orange solid (90 mg,

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yield of 87%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$) 9.29 (d, 2H), 9.18 (d, 2H), 8.83 (d, 4H), 8.80 (d, 2H), 8.44 (d, 4H), 4.51 (s, 6H)

2,2'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn] [3,8] phenanthroline-2,7-diyl)bis(1-methylpyridin-1-ium) (DM-N2-NDI2I)

In a dry 2 neck round bottom flask, **DPy-N2-NDI** (91 mg, 0.18 mmol) was added into DMAc (20 ml), then iodomethane (0.25 g, 1.8 mmol) was added into the solution dropwise. After heating at 90 °C for 24 hr, the reaction was cooled to room temperature and the precipitation was collected by filtration and washed with 20 ml of cold ethyl ether. The pure compound was obtained as an orange solid (70 mg, yield of 67%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$) 9.38 (d, 2H), 8.97 (t, 2H), 8.87 (d, 4H), 8.59 (m, 2H), 8.44 (m, 2H), 4.39 (s, 6H)

4,4'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn][3,8] phenanthroline-2,7-diyl)bis(1-hexylpyridin-1-ium) (DH-N4-NDI2Br)

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In a dry 2 neck round bottom flask, **DPy-N4-NDI** (182 mg, 0.36 mmol) was added into DMAc (20 ml), then 1-bromohexane (0.3 g, 1.81 mmol) was added into the solution dropwise. After heating at 90 °C for 24 hr, the reaction was cooled to room temperature and the precipitation was collected by filtration and washed with 20 ml of cold ethyl ether. The pure compound was obtained as a yellow solid (143 mg, yield of 67%). ¹H NMR (300 MHz, DMSO-*d*₆) 9.38 (d, 4H), 8.83 (d, 4H), 8.39 (d, 4H), 4.72 (d, 2H), 2.02 (m, 4H), 1.32 (m, 8H), 0.89 (t, 6H)

3,3'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8] phenanthroline-2,7-diyl)bis(1-hexylpyridin-1-ium) (**DH-N3-NDI2Br**)

In a dry 2 neck round bottom flask, **DPy-N3-NDI** (182 mg, 0.36 mmol) was added into DMAc (20 ml), then 1-bromohexane (0.3 g, 1.81 mmol) was added into the solution dropwise. After heating at 90 °C for 24 hr, the reaction was cooled to room temperature and the precipitation was collected by filtration and washed with 20 ml of cold ethyl ether. The pure compound was obtained as a yellow solid (127 mg, yield of 60%). ¹H NMR (300 MHz, DMSO-*d*₆) 9.29 (d, 2H), 9.18 (d, 2H), 8.83 (d, 4H), 8.80 (d, 2H), 8.44 (d, 4H), 4.72 (d, 2H), 2.02 (m, 4H), 1.32 (m, 8H), 0.89 (t, 6H)

Chapter 2. Electrochromic naphthalene diimides compounds

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2.5. Reference

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Chapter 2. Electrochromic naphthalene diimides compounds

**Chapter 3. Synthesis and Characterization of Cross-linkable tetraphenyl
benzidine-based monomers for Use in Electrochromic devices**

3.1. Introduction

Triphenyl amine (TPA), which has a propeller structure, and its derivatives are promising candidates in various organic electronic devices, such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), perovskite solar cells (PSCs), and electrochromic devices (ECDs).^{1,2} It is well known that TPA undergoes a one-electron oxidation to form TPA cation radicals under external voltage.³ However, TPA cation radicals are easily dimerized or react with TPA monomer to form tetraphenyl benzidine (TPB), which is more easily oxidized and undergoes further oxidation. Upon anodic oxidation, TPA based polymers exhibits reversible color change from transparent to multi colors including yellow, green, blue and purple.

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Scheme 3. 1. Anodic oxidation pathways of TPA and TPB

The color change of TPA copolymer is tunable by appropriate choice of substituents on TPA moieties and the other monomer for copolymerization.⁴ To date, various TPA based amines have been developed by Liou group, and they were copolymerized with different sorts of aromatic diacids to form TPA containing polyamides.^{5–10} For example, in 2016, Liou *et al.* incorporated methyl substituted TPA amines and dicarboxylic acid containing aromatic monomers (terephthalic acid, isophthalic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-dicarboxydiphenyl ether, 4,4'-sulfonyldibenzoic acid, 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane, 1,4-naphthalenedicarboxylic acid, and 2,6-naphthalenedicarboxylic acid) to form alternating copolymers.¹¹ They obtained a series of polyamides with good solubility in polar organic solvent, thermal stability and reversible color change from pale yellow to green (oxidized) as shown in Figure 3.1.

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Scheme 3. 2. Synthesis of TPA containing polyamides

Figure 3. 1. a) UV absorbance of poly (3,5-dimethyl-4',4''-diaminotriphenylamine-co-4,4'-dicarboxydiphenyl ether); b) CV of poly (3,5-dimethyl-4',4''-diaminotriphenylamine-co-4,4'-dicarboxydiphenyl ether)

The electropolymerization of indole was pioneered back in 1982 by F. Garnier *et al.* in non-aqueous solvent.¹² Lately, in 1998, A. Bagheri reported indole electropolymerization in various acidic solutions including HClO₄, H₂SO₄, HCl, H₃PO₄ and CHCOOH.¹³ Among the probable coupling sites on indole, they demonstrated the most possible way is 1,3-coupling as shown in Figure 3.2. typical CV spectra is shown in Figure 3.2 (b), the increasing currency through out the system indicates the success of electro polymerization of indole. Polyindole film exhibits color change from yellow (undoped state) to green (doped state).¹⁴ Integrating indole as the crosslinking group with TPA allows direct polymerization on transparent

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electrode, moreover, polymerized indole may change the optical and electrochromic properties of TPA.

Figure 3. 2. a) Probable coupling sites of indole; b) Typical cyclic voltammetry of indole in HClO4

In this research, indole modified tetraphenylenebenzidines were synthesized though the cross-coupling reaction between N, N'-diphenylbenzidine and corresponding indole modified precursors. Resulted products are characterized by ¹H-NMR and ¹³C-NMR.

3.2. Results and discussion

3.2.1. Synthesis of indole precursor

1-(6-Bromo-hexyl)-1H-indole (1) and 6-Bromo-1-hexyl-1H-indole (4) were synthesized in this research as the indole precursors base on the work reported by D. Zhu *et al.* reported in 2009.¹⁵ For compound (1), Excessive 1,6-dibromohexane was used to prevent the formation of disubstituted indole. NaOH was stirred with indole as the deprotonating reagent before 1,6-dibromohexane was added. The synthetic route to compound (1), (2) and (4) are depicted in Scheme 3.3.

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The ^1H -NMR of 1-(6-Bromo-hexyl)-1H-indole (1) and 6-Bromo-1-hexyl-1H-indole (4) are consistent with the structure of corresponding product as show in Figure 3.3. The new proton resonance peak around 4.1 ppm belongs to the aliphatic proton on the carbon atom which directly connected to the nitrogen on indole.

Figure 3. 3. ^1H -NMR of 1-(6-Bromo-hexyl)-1H-indole (1) and 6-Bromo-1-hexyl-1H-indole (4)

1-[6-(4-Bromo-benzyloxy)-hexyl]-1H-indole (2) was obtained by following a similar method. Figure 3.4 displays the ^1H -NMR of compound (2). The observed proton resonances are consistent with the structure of compound (2).

Figure 3. 4. ¹H-NMR of 1-[6-(4-Bromo-benzyloxy)-hexyl]-1H-indole (2)

Scheme 3. 3. Synthetic route of compound (1), (2) and (4)

1-[6-(4-Bromo-benzyloxy)-hexyl]-1H-indole (2) and 6-Bromo-1-hexyl-1H-indole (4) are readily soluble in polar solvents including acetone, acetonitrile and methanol.

3.2.2. Synthesis of N4, N4'-bis(4-(((6-(1H-indol-1-yl) hexyl) oxy) methyl) phenyl)-N4,N4'-diphenyl-

phenyl)-N4,N4'-diphenyl-[1,1'-biphenyl]-4,4'-diamine and 4,4'-bis((1-hexyl-1H-indol-6-yl)(phenyl)methyl)-1,1'-biphenyl

N4, N4'-bis(4-(((6-(1H-indol-1-yl) hexyl) oxy) methyl) phenyl)-N4,N4'-diphenyl-[1,1'-biphenyl]-4,4'-diamine and 4,4'-bis((1-hexyl-1H-indol-6-yl)(phenyl)methyl)-1,1'-biphenyl are synthesized by using indole precursors (compound (2) and (4)) and N, N'-diphenylbenzidine through Buchwald-Hartwig coupling reaction as show in Scheme 3.4 and 3.5. In addition to the synthetic details, the structures of target products were confirmed by ¹H-NMR and ¹³C-NMR as shown in Figure S. 18 and Figure S. 20.

Scheme 3. 4. Synthetic route of N4, N4'-bis(4-(((6-(1H-indol-1-yl) hexyl) oxy) methyl) phenyl)-N4,N4'-diphenyl-[1,1'-biphenyl]-4,4'-diamine

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Scheme 3. 5. Synthetic route of 4,4'-bis((1-hexyl-1H-indol-6-yl) (phenyl)methyl)-1,1'-biphenyl

3.3. Conclusion

N4, N4'-bis(4-(((6-(1H-indol-1-yl) hexyl) oxy) methyl) phenyl)-N4,N4'-diphenyl-[1,1'-biphenyl]-4,4'-diamine and 4,4'-bis((1-hexyl-1H-indol-6-yl)(phenyl)methyl)-1,1'-biphenyl are synthesized with good solubility. Indole moiety in each compound works as cross linkable group for electropolymerization in solution. Modified TPB chromophores are ready for film deposition on ITO directly through electropolymerization.

3.4. Experimental

Materials and instrumental

1-(6-Bromo-hexyl)-1H-indole, 1,6-Dibromohexane, 1-Bromohexane, N, N'-diphenylbenzidine, Tris-(dibenzylideneacetone)-dipalladium (0) ($\text{Pd}(\text{dba})_3$), tri-tert

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Butylphosphane were purchased from Sigma-Aldrich. CA. 4-Bromo Benzyl alcohol and 6-Bromo-1H-indole were purchased from Combi Block. US.

Toluene and N, N'-Dimethyl methanamide were dried and distilled over CaH_2 under an atmosphere of dry argon. Chloroform, Hexane and Acetone were obtained as reagent degree and used directly.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance Digital 300 and 400 MHz (300 and 75 MHz for ^1H and ^{13}C NMR). Resonances were quoted on the δ scale relative to tetramethylsilane (TMS, $\delta = 0$) as an internal standard. For ^1H -NMR spectra, the following abbreviations have been used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared measurements were performed on a Varian 1000 FT-IR Scirinitar series spectrophotometer. The following abbreviations have been used in IR spectra: s = strong, m = medium, w = weak, br. = broad, sh = sharp. The measuring mode was %T (percentage transmittance). The bands were expressed in cm^{-1} (per centimeter).

Synthesis of 1-(6-Bromo-hexyl)-1H-indole (1)

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A mixture of indole (2.50g, 21.3mmol), NaOH (1.43g, 25.56mmol) and 1,6-dibromohexane (15.62g, 64.2mmol) in DMF (100ml) was stirred at room temperature for 48h under argon. The reaction mixture was diluted with water (100ml) and extracted with chloroform (25ml x 3). The combined organic phase was washed with brine, dried with MgSO₄, and concentrated. The residue was purified by chromatography with hexane-acetone (19:1). The product is a pale green oil. Yield: 4.51g, 76%. ¹H NMR (300 MHz, Chloroform-d) δ 7.72 – 7.63 (m, 1H), 7.38 (dq, J = 8.2, 0.9 Hz, 1H), 7.30 – 7.19 (m, 1H), 7.18 – 7.08 (m, 2H), 6.53 (dd, J = 3.1, 0.8 Hz, 1H), 4.16 (t, J = 7.0 Hz, 2H), 3.41 (t, J = 6.7 Hz, 2H), 1.98 – 1.78 (m, 4H), 1.59 – 1.43 (m, 2H), 1.36 (dddd, J = 14.0, 8.7, 5.8, 1.6 Hz, 2H)

Synthesis of 1-[6-(4-Bromo-benzyloxy)-hexyl]-1H-indole (2)

Compound 1 (1g, 3.5mmol) and 4-bromo benzyl alcohol (1.5g, 8mmol) were added into a flask and dissolved in toluene (20ml). KOH (0.5g, 8.9mmol) was dissolved in 5ml of water, then added into the flask. A tip of tetrabutylammonia bromide was added into the system. The reaction was heated up to 90 degrees under nitrogen overnight then cooled down to r.t. 100 mL of water was added into the flask to dilute the solution. The solution was extracted by CHCl₃ (10ml x 3). The combined organic layer was dried with brine and sodium sulfate. Then the residue was purified

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by column with hexane and acetone (9:1). Yield: 1.01g, 75%. ¹H NMR (300 MHz, Chloroform-d) δ 7.65 (dt, J = 7.8, 1.0 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.35 (dq, J = 8.3, 0.9 Hz, 1H), 7.26 – 7.16 (m, 3H), 7.15 – 7.07 (m, 2H), 6.50 (dd, J = 3.1, 0.8 Hz, 1H), 4.43 (s, 2H), 4.13 (t, J = 7.1 Hz, 2H), 3.44 (t, J = 6.4 Hz, 2H), 1.86 (p, J = 7.2 Hz, 2H), 1.59 (d, J = 10.9 Hz, 2H), 1.49 – 1.25 (m, 4H)

Synthesis of N4, N4'-bis(4-(((6-(1H-indol-1-yl) hexyl) oxy) methyl)phenyl)-N4,N4'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (3)

Tris(dibenzylideneacetone)dipalladium (0) ($\text{Pd}(\text{dba})_3$) (0.175g, 10%equiv, 0.20 mmol) and tri-tert butylphosphane (0.35ml, 0.35mmol, 1M) were dissolved under nitrogen in 40 mL of dry toluene and stirred for 10 min at room temperature. The catalyst was then added to a mixture of N,N'-diphenylbenzidine (0.5 g, 1.5 mmol), 1-[6-(4-Bromo-benzyloxy)-hexyl]-1H-indole (1.4 g, 3.6 mmol) and sodium-tert-butyloxide (0.5g, 5.2 mmol) in 30 mL of toluene. The reaction mixture was stirred for 6 h at 90 °C. After cooling to ambient temperature, the solution was diluted with 100 mL of toluene, and washed with water. After removing the solvent, the residue was purified by flash chromatography on silica gel with hexane and acetone (4:1). The product was obtained as a dark yellow oil. Yield: 1.29g, 91%. ¹H NMR (300 MHz,

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Chloroform-d) δ 7.64 (dt, J = 7.8, 1.0 Hz, 2H), 7.53 – 7.41 (m, 4H), 7.36 (d, J = 8.2 Hz, 2H), 7.31 – 7.17 (m, 12H), 7.13 (ddd, J = 8.4, 4.2, 1.6 Hz, 16H), 6.50 (dd, J = 3.1, 0.9 Hz, 2H), 4.44 (s, 4H), 4.14 (t, J = 7.1 Hz, 4H), 3.49 (t, J = 6.5 Hz, 4H), 1.88 (p, J = 7.2 Hz, 4H), 1.62 (q, J = 6.7 Hz, 4H), 1.52 – 1.29 (m, 6H). ^{13}C NMR (75 MHz, Chloroform-d) δ 147.65 , 146.67 , 134.74 , 132.90 , 129.24 , 128.86 , 127.76 , 127.27 , 124.29 , 124.11 , 124.06 , 122.84 , 121.29 , 120.92 , 119.14 , 109.34 , 100.85 , 77.22 , 72.63 , 70.32 , 46.32 , 30.19 , 29.59 , 27.10 , 26.83 , 25.89 .

Synthesis of 6-Bromo-1-hexyl-1H-indole (4)

To a flask under argon, 6-Bromo-1H-indole (5 g, 0.025 mol) and KOH (4.5 g, 1.1equiv) were added and dissolved in dry DMF (50 ml). The reaction was heated up to 50°C under argon for 24h. Then the mixture was diluted by water (200 ml) and extracted with chloroform (30 ml x 5). The combined organic layer was dried with brine and sodium sulfate. Then the residue was purified by column with hexane.

Yield: 5.80g, 81%. ^1H NMR (300 MHz, Chloroform-d) δ 7.49 (d, J = 8.2 Hz, 2H),

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7.20 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.08 (d, $J = 3.1$ Hz, 1H), 6.47 (dd, $J = 3.1, 0.9$ Hz, 1H), 4.08 (t, $J = 7.2$ Hz, 2H), 1.83 (p, $J = 7.1$ Hz, 2H), 1.39 – 1.24 (m, 6H), 0.96 – 0.81 (m, 3H).

Synthesis of 4,4'-bis((1-hexyl-1H-indol-6-yl)(phenyl)methyl)-1,1'-biphenyl (5)

Tris(dibenzylideneacetone)dipalladium (0) ($\text{Pd}(\text{dba})_3$) (0.175 g, 10%equiv, 0.20 mmol) and tri-tert butylphosphane (0.35 ml, 0.35 mmol, 1M) were dissolved under nitrogen in 40 mL of dry toluene and stirred for 10 min at room temperature. The catalyst was then added into a mixture of N, N'-diphenylbenzidine (0.5 g, 1.5 mmol), 6-Bromo-1-hexyl-1H-indole (1g, 3.6mmol) and sodium-tert-butyloxide (0.5 g, 5.2 mmo) in 30 mL of toluene. The reaction mixture was stirred for 6 h at 90 OC. After cooling to ambient temperature, the solution was diluted with 100 mL of toluene, and washed with water. After removing the solvent, the residue was purified by flash chromatography on silica gel with hexane and acetone (4:1). The product was obtained as a yellow oil. Yield: 1.02g, 93%. ^1H NMR (400 MHz, Chloroform-d) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.47 – 7.40 (m, 4H), 7.30 – 7.20 (m, 4H), 7.18 – 7.12 (m, 10H), 7.08 (d, $J = 3.0$ Hz, 2H), 7.01 – 6.90 (m, 4H), 6.47 (d, $J = 3.1$ Hz, 2H), 3.99 (t, J

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= 7.1 Hz, 4H), 1.76 (t, $J = 7.1$ Hz, 4H), 1.35 – 1.17 (m, 12H), 0.94 – 0.78 (m, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 148.42, 142.02, 136.77, 133.86, 128.96, 127.92, 126.93, 125.47, 123.05, 122.98, 121.68, 121.55, 119.20, 107.35, 100.90, 46.28, 31.39, 30.93, 30.18, 26.59, 22.48, 13.99.

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3.5. Reference

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Appendix A IR and CV data

Figure. S. 1. IR of DPy-N2-NDI

Figure. S. 2. IR of DPy-N3-NDI

Figure. S. 4. CV of DM-N4-NDI-2I

Figure. S. 5. CV of DM-N3-NDI-2I

Figure. S. 6. CV of DM-N2-NDI-2I

Figure. S. 7. CV of DH-N4-NDI-2Br

Figure. S. 8. CV of DH-N3-NDI-2Br

Appendix B ¹H-NMR

Figure. S. 9. ¹H-NMR of DPy-N2-NDI

Figure. S. 10. ^1H -NMR of DPy-N3-NDI

Figure. S. 11. ^1H -NMR of DPy-N4-NDI

Figure. S. 12. ^1H -NMR of DM-N2-NDI-2I

Figure. S. 13. ^1H -NMR of DM-N3-NDI-2I

Figure. S. 14. ^1H -NMR of DM-N4-NDI-2I

Figure. S. 15. ^1H -NMR of DH-N4-NDI-2Br

Figure. S. 16. ¹H-NMR of 1-(6-Bromo-hexyl)-1H-indole

Figure. S. 17. ¹H-NMR of 1-[6-(4-Bromo-benzyloxy)-hexyl]-1H-indole

Figure. S. 18. ^1H -NMR of N_4, N_4' -bis(4-(((6-(1H-indol-1-yl) hexyl) oxy) methyl)phenyl)- N_4, N_4' -diphenyl-[1,1'-biphenyl]-4,4'-diamine

Figure. S. 19. ^1H -NMR of 6-Bromo-1-hexyl-1H-indole

Figure. S. 20. ¹H-NMR of 4,4'-bis((1-hexyl-1H-indol-6-yl)(phenyl)methyl)-1,1'-biphenyl