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Indoloquinoxaline as a Terminal Building Block for the Construction of π -

Conjugated Small Molecules Relevant to Organic Electronics

Abby-Jo Payne,¹ Jenny S. J. McCahill² and Gregory C. Welch^{*1}

Department of Chemistry, Dalhousie University, 6274 Coburg Road, P.O. Box 15000, Halifax, Nova Scotia, Canada, B3H 4R2

¹ Current Address: Department of Chemistry, University of Calgary, 731 Campus Place N.W. Calgary, AB, Canada T2N 1N4

²Current Address: Carbon Engineering Ltd. 3535 Research Road NW, Calgary, AB, Canada, T2L 2K8

* Corresponding Author

Email: gregory.welch@dal.ca / gregory.welch@ucalgary.ca

Phone Number: 1 (403)-210-7603

Abstract: Herein we introduce the π -conjugated organic building block, 8-bromo-indolo[2,3b]quinoxaline (indoloquinoxaline, **IQ**), that combines both electron withdrawing and donating nitrogen atoms. It is accessible from low-cost starting materials through a straightforward and high yielding condensation reaction. In terms of materials design, indoloquinoxaline is suitable for use as a terminal unit; it can act as a planar extension of the π -conjugated system and is easily functionalized with aliphatic side-chains, which can alter material solubility and self-assembly processes. The indoloquinoxaline framework is highly versatile and can be readily derivatized considering the hundreds of commercially available indole and phenylenediamine starting materials. In this case, the indoloquinoxaline building block is neither strongly electron rich or deficient which allows for material optoelectronic properties to be largely dictated by the character of the molecular core, as shown through the incorporation of three different core units, a weak thiophene donor, a strong benzodithiophene donor and an isoindigo acceptor.

Keywords: Organic Electronics, Conjugated Small Molecules, Indoloquinoxaline, Isoindigo, Benzodithiophene, Thiophene,

Highlights:

Introduction of a new indoloquinoxaline organic π -conjugated building block Simple synthesis of functionalized indoloquinoxaline building blocks Synthesis of three new chromophores with progressively red-shifted band gaps

1. Introduction

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Organic π -conjugated small molecules have found wide spread applications in a range of electronic devices. One of the most well-known is their use as donor and acceptor components in organic solar cells (OSC).[1–9] π -conjugated small molecules have also been employed as light harvesters in metal-free dye sensitized solar cells (DSSC),[10–13] semiconducting materials in organic field effect transistors (OFETS),[14–17] and as hole transporting materials in both DSSC and perovskite solar cells (PSC).[18–23]

The solution-processability of these materials is key to their practical application, enabling them to be printed or coated onto lightweight, flexible substrates, which in turn allows for easy storage, transportation and installation measures.[24–30] While great improvements in device performance have been realized over the past few years,[31,32] there is a need for new and improved optoelectronic materials.[33,34] Key to the growth of organic electronics towards commercialization is the development of cost-effective organic π -conjugated materials that can be readily accessible from raw materials, through a sustainable synthesis with scalable purification.[24,35,36]

The utility of low-cost building blocks for organic electronics is dictated by their functional versatility. Specific π -conjugated organic building blocks are integrated within the molecular framework to tune the optoelectronic properties and the self-assembly tendencies of the material. One of the key design principles for π -conjugated materials is based on band-gap engineering. From a molecular design perspective, this can commonly be done in three ways: (1) increasing the conjugation length,[37,38] (2) incorporation of electron-donating/withdrawing moieties and (3) the intramolecular donor-acceptor (D-A) approach.[39–41] From this perspective

we have synthesized a novel highly tunable π -conjugated building block for use in organic electronics.

The 8-bromo-indolo[2,3-b]quinoxaline (IQ) building block is a π -conjugated planar framework accessible from inexpensive, readily available precursors. The base indoloquinoxaline structure offers several avenues for structural versatility relevant to organic electronic applications. The electronic and self-assembly tendencies of this building block can be tuned by the incorporation of various functionalized o-phenylenediamines with over 500 monosubstituted and more than 300 di-substituted commercially available derivatives. Furthermore, the amido nitrogen can be functionalized with aliphatic side chains, facilitating adequate solution processability and potentially dictating self-assembly propensities. Indologuinoxaline derivatives are well known and actively studied in medicinal chemistry for their antiviral and anticancer properties.[42–44] Only recently have they been explored as building blocks for use in organic electronics including their incorporation into OLEDS and DSSCs. These indoloquinoxaline derivatives, similar to our reported material but with functionalization occurring through the 9-position, have been successfully incorporated into small molecule architectures and have exhibited potential for application in organic electronics. [45-48]

In this study we utilized *o*-phenylenediamine with 6-bromoisatin to access a unique building block, **IQ**, which is employed as an end-capping unit to effectively extend the π conjugation and promote a planar framework. In the context of strongly electron donating and
electron accepting building blocks, **IQ** can be described as electron neutral, as it contains both
electron donating and electron withdrawing nitrogen atoms. This neutral character is a result of
the pyrazene nitrogen lone pairs being orthogonal to the π -system, and therefore their

contribution is solely an inductive one, withdrawing electron density from the π -system, which leads to a slight electron-accepting character. The latter is countered by the weak electron donation from the indole π -conjugated ring. These competing effects are thought to render the building block neither strongly electron donating or accepting. To study the effect of this new building block on the optoelectronic properties of a π -conjugated system, three core building blocks were selected with differing electronic character, a weakly donating thiophene unit (**Th**), a strongly donating benzodithiophene unit (**BDT**) and an electron accepting isoindigo core (**H**(**Th**)₂).

2. Results and Discussion

2.1 Synthesis

The acid catalyzed condensation of indoloquinoxaline from isatin and *o*-phenylenediamine has been previously outlined in the literature (**A**);[42,49,50] however, upon the introduction of electron withdrawing groups on the isatin analog, an alternative product is observed. The reaction intermediate is shifted towards the cleavage of the isatin ring, forming the ring opened species as depicted in **B**.[50] Upon heating a 1:1 mixture of 6-bromoisatin and *o*-phenylenediamine at reflux in acetic acid, a yellow precipitate was formed after 30 minutes. Presumed to be the mono-condensation product, dimethylformamide (DMF) was added to the mixture allowing for a higher reflux temperature. This in turn, led to the re-dissolution of the precipitate was observed. The material was cooled to room temperature and a yellow/brown precipitate was observed. The material was collected *via* vacuum filtration and washed with copious amounts of water followed by a 1:1 H₂O:EtOH solution. Using this modified literature procedure (**C**), the product 8-bromo-indolo[2,3-b]quinoxaline (**IQ**) was successfully synthesized

and isolated as an off-white powder in high yields (< 80 %) with relatively high purity. **IQ** was subsequently used without any further purification in a *N*-alkylation reaction with octylbromide in the presence of base (K_2CO_3) in DMF to generate 8-bromo-N-octyl-indolo[2,3-*b*]quinoxaline (**IQ-Oct**) (**D**). Upon reaction of all starting material, as monitored by thin layer chromatography (TLC), the mixture was cooled to room temperature and stirred in a 1:1 solution of H₂O/MeOH and which resulted in the precipitation of **IQ-Oct** as a bright orange solid. The material was recovered *via* suction filtration and washed with copious amounts of water followed by a 1:1 H₂O/MeOH solution. The final yield of the alkylated product was 84 % with no further purification required. Both new compounds **IQ** and **IQ-Oct** were characterized by ¹H and ¹³C NMR spectroscopy and identified by atmospheric pressure chemical ionization (APCI) mass spectrometry.

The mono-brominated **IQ** building block is ideally suited for incorporation as a terminal end-capping unit. Carbon-carbon bond forming reactions were accomplished similar to our previously published methods with the use of the heterogeneous catalyst Silia*Cat*® DPP-Pd.[51–53] Final compounds **1** and **2** were prepared by a Stille coupling between the bis-stannylated cores and two equivalents of **IQ-Oct** under microwave irradiation, while compound **3** was synthesized through the direct heteroarylation of 6,6'-di(thiophen-2-yl)-1,1'-di(octyl)isoindigo with two equivalents of **IQ-Oct** under conventional heat (Figure 3). Conventional heating was used for the direct heteroarylation reaction due to the result of multiple substitutions occurring on the thiophene obtained upon microwave irradiation as seen in our previous work.[53]

The work up for compounds **1** and **2** involved stirring the completed reaction mixtures in methanol and collecting the resultant orange solid *via* suction filtration. The materials were then dissolved in dichloromethane and solution filtered to remove the Silia*Cat*® DPP-Pd heterogeneous catalyst. The solvent was removed under reduced pressure, the materials slurried in methanol, and the resultant products were collected *via* suction filtration washing with ethanol and isopropanol. For compound **3**, the reaction mixture stirred in a 1:1 H₂O:MeOH solution and the resultant fine black powder was isolated by suction filtration and washed with water, methanol, and ethanol. The product was further purified by flash column chromatography with chloroform as the eluent. Compound **3** was isolated with 55 % yield. Compound **1** was characterized by ¹H and ¹³C NMR spectroscopy and identified by CHN elemental analysis.

2.2 Optical Properties

The UV-Vis absorption spectra of the final compounds were obtained from 1% wt/v solutions in chloroform, both solution and thin-film absorption profiles are shown in Figure 4 and the data is summarized in Table 1. The **IQ** terminal units are neither strongly electron donating or accepting, thus the optical properties are predominately determined by the extended π -conjugation and the nature of core building block. Compound **1** primarily absorbs light in the blue region of the visible spectrum with λ_{onset} at ~492 nm in solution. A small electron delocalization pathway and lack of D-A character limit light absorption to high energy photons. Compared to compound **1** with a thiophene core, compound **2** with the **BDT** core has an extended π -conjugated framework and leads to a red-shift in absorbance with a λ_{onset} at ~525

solution. Compound **3** highlights the benefit of using a strongly absorbing dye as well as the D-A approach to bandgap engineering as the D-A character of the thiophene-flanked isoindigo core further narrows the bandgap, resulting in an absorption spectra extending beyond 700 nm. Upon transitioning from solution to thin-film, a bathochromic shift in the absorption profile is observed for each of the three molecules indicating intermolecular interactions in the solid-state. The more pronounced low energy band visible in both solution and thin film of compound **2** is likely a result of stronger intermolecular π - π interactions compared to compound **1**. The photoluminescence was also measured for compounds **1**–**3**. Compound **1** has a small Stokes shift of 43 nm, where as **2** and **3** have relatively larger Stokes shift of 141 nm 125 nm respectively, a result of their increased conformational flexibility.

The electronic character of IQ is further highlighted upon comparing compounds 1-3 with reference compounds in the literature (Figure 5). Compound 1 has a very comparable absorption profile to that of a similar compound Phth-Th-Phth, which is comprised of a thiophene core end capped with alkylated phthalimides.[54–56] The onset of Phth-Th-Phth in solution is 440 nm with an absorption max centered at 390 nm compared to 492 nm and 430 nm for compound 1. Although 1 has a significantly extended π -conjugated pathway (9 units vs. 3 units) the absorption profile is only red-shifted by less than 50 nm. Only a slight red-shift is observed for 1 with its extended conjugation as it lacks the D/A character of Phth-Th-Phth which would lead to more dramatic shift. Phthalimide is an electron acceptor and when paired with the donor thiophene core results in a D/A type system. Alternatively, for compound 1 the bandgap is primarily dictated by the length of the π -conjugated backbone with no significant D/A intramolecular interaction which would lead to a further red shift in absorption. Compound

2 can be compared to the previously reported **DO1**[57], which is comprised of a BDT core with electron accepting indandione endcaps bridged with alkyl thiophenes. Despite a similar conjugation length to **2**, the D/A character of **DO1** leads to a significant red shifted (~125 nm) absorption spectra as a result of the interaction between the strongly electron donating BDT core and the strong terminal acceptor indandione. We can compare compound **3** with two different isoindigo dithiophene compounds in the literature, **Oct-II**(**ThPhth-1EP**)₂[53] which has terminal electron accepting phthalimide units and **II**(**Th**₂)₂[58] which is end-capped with electron donating hexyl-bithiophenes. The absorption profile of compound **3** with the **IQ** terminal units lies appropriately in between the two, but slightly closer to that of **II**(**Th**₂)₂. The onset of absorption for **3** is slightly red shifted from the **II**(**ThPhth-1EP**)₂ with electron withdrawing endcaps and is slightly blue shifted from **II**(**Th**₂)₂ with electron donating end caps. Thus, based on these comparisons, the **IQ** unit can be thought of neither strongly electron donating or withdrawing and can be used to effectively extend the size of the molecular structure without dramatically altering the electron structure through D-A type electronic coupling.

2.3 Electrochemical Properties

The electrochemical properties of compounds 1-3 were investigated using cyclic voltammetry (CV) and were found to be largely dominated by the nature of the core unit. The highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energy levels were measured from the onset of oxidation and reduction respectively relative to the internal reference ferrocene. As shown in Figure 6, each compound has reversible oxidations while only **3** has a reversible reduction, attributed to the electron accepting nature of the isoindigo core. The lack of reversible reductions for **1** and **2** is reasonable, as a result of their electron rich character. Considering the ionization potential (IP) of the two electron-donating

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cores, the substitution of **Th** for a **BDT** core is accompanied by a decrease in the IP of the compound highlighting the more electron-rich nature of compound 2. On the other hand, monitoring the change in electron affinity (EA) is more suitable for the $II(Th)_2$ core substitution, which demonstrates a greater EA than compounds 1 and 2, a result of the electron-withdrawing character of the isoindigo core. Another noticeable trend for compound 1–3 is the narrowing of the band gap, which is consistent with the increase in effective conjugation length.

2.4 Theoretical Modeling

Theoretical calculations were used to investigate optimized geometry (gas phase), electronic structure, and electronic transitions of the three new chromophores with IQ terminal units (Figure 7), see ESI for full computational methods. The molecular core dictates the planarity of the structure, with $II(Th)_2$ being the least distorted backbone, followed by BDT and lastly Th. Although the π -conjugated backbone of compound 1 is slightly distorted, the predicted HOMO and LUMOs are fully delocalized along the entire structure indicating good

electronic communication between the **Th** and **IQ** units. Upon transitioning from the relatively weakly donating **Th** core to the relatively strongly donating **BDT** core, the LUMO remains fully delocalized; however, the HOMO is appropriately localized on the strong electron-donating core, with limited contribution from the terminal **IQ** units. With the incorporation of the electron accepting isoindigo core, the **IQ** terminal unit does not contribute to either the HOMO or LUMO delocalized π -systems. The LUMO is largely localized at electron deficient isoindigo core, while the HOMO π -system does not extend past the indole ring of the **IQ** end cap. These depictions of the ground state geometry and π -system lend further evidence that the **IQ** unit is nether electron rich or poor and can be consider electron neutral, and highlight the overwhelming influence of the core on all facets of material properties. The predicted HOMO/LUMO energy levels and absorption profile for the three small molecules follow the same trend observed experimentally with progressively red-shifted band gaps; however, in the case of the **3** it was the higher energy band that was more prominent, not the low energy band as predicted by TD-DFT.

3 Conclusions

In this study we reported the synthesis of 8-bromo-6*H*-indolo[2,3-*b*]quinoxaline (**IQ**), a novel building block for application in organic electronics. **IQ** is easily accessible from inexpensive starting materials and a sustainable high yielding synthesis. The **IQ** building block was found to be useful as an end-capping unit for the construction of organic π -conjugated small molecules. The **IQ** building block was found to be neither strongly electron rich nor poor and can be considered an electron neutral unit. **IQ** is effective for the extension and planarization and of π -conjugated systems and for allowing the material properties to be dictated by the nature of the core building block. The versatility of the framework and the wealth of available substituted

phenylenediamines and indoles can be exploited to tailor the electronic properties of this terminal unit to the desired effect.

4 Experimental

Full experimental details including materials and methods, instrumentation, and NMR spectra can be found in the supporting information.

4.1 Synthesis of 8-bromo-6H-indolo[2,3-b]quinoxaline (IQ).

A solution of 6-bromoisatin (1.123 g, 4.5 mmol) and *o*-phenylenediamine (0.722 g 6.7 mmol) in glacial acetic acid (30 mL) was refluxed for 30 minutes when a significant amount of yellow precipitate was observed. DMF (30 mL) was added to the mixture, the temperature was increased to 150°C and the reaction was allowed to stir at reflux for 24 hours. The dark red/brown solution was cooled to room temperature and a yellow/brown precipitate was observed. The material was collected via vacuum filtration and washed with copious amounts of water followed by ~100 mL of 1:1 H₂O:Et₂OH solution. The solid was dried *in vacuo* to yield 1.205 g (81 % yield) of the product as a light yellow powder. ¹H NMR (300MHz, DMSO-d₆, ppm): δ 7.51 (dd, ¹J= 9.9 Hz, ²J= 1.5 Hz, 1H), 7.71-7.85 (m, ov, 3H), 8.06 (dd, ¹J= 9.3 Hz, ²J= 1.2 Hz 1H), 8.23 (dd,¹J= 9.6 Hz, ²J= 1.2 Hz, 1H), 8.27 (d, J=8.1 Hz, 1H). ¹³C{¹H} NMR (300MHz, DMSO-d₆, ppm): δ 114.9, 118.2, 124.0, 124.1, 124.5, 126.7, 127.7, 138.8, 139.1, 140.3, 144.9, 146.0. Mass Spec: Theoretical: 298.1, Experimental: 298.0

4.2 Synthesis of 8-bromo-N-octyl-indolo[2,3-b]quinoxaline (IQ-Oct).

A solution of 8-bromo-indolo[2,3-*b*]quinoxaline (0.40 g, 1.34 mmol), K_2CO_3 (0.28 g, 2.02 mmol), 1-octylbromide (0.3 mL, 1.34 mmol) in anhydrous DMF (5 mL) was heated to 100°C for 16 hours in a 20 mL pressure tube capped under N₂. The reaction was cooled to room temperature and poured into a 1:1 solution of H₂O/MeOH (~100 mL) and stirred for two hours.

A bright orange solid was recovered via suction filtration. The solid was washed with copious amounts of water followed by ~100 mL 1:1 H₂O/MeOH solution. The solid was dried *in vacuo* to give 0.46 g (84% yield) of the alkylated product. ¹H NMR (300MHz, CDCl₃, ppm): δ 0.88 (t, 3H), 1.25-1.31 (m, br, 6H), 1.39-1.40 (m, br, 4H), 1.91-2.00 (m, 2H), 4.47 (t, 2H), 7.55 (dd, ¹*J*= 9.8 Hz, ²*J*= 1.6 Hz, 1H), 7.65 (d, *J*= 1.5 Hz, 1H), 7.68-7.79 (m, ov, 2H), 8.15 (dd, ¹*J*= 9.6 Hz, ²*J*= 1.3 Hz, 1H), 8.30 (dd, ¹*J*= 9.7 Hz, ²*J*= 1.3 Hz, 1H), 8.34 (d, *J*= 8.3 Hz, 1H). ¹³C{¹H} NMR (300MHz, CDCl₃, ppm): δ 14.0, 22.6, 27.0, 28.4, 29.1, 29.2, 31.8, 41.6, 112.8, 118.4, 123.8, 124.0, 125.1, 126.3, 128.0, 129.0, 129.4, 139.5, 140.7, 145.7. Mass Spec: Theoretical: 410.4, Experimental: 410.0

4.3 Synthesis of 2,5-bis(6-octyl-6H-indolo[2,3-b]quinoxalin-8-yl)thiophene (1).

8-bromo-N-octyl-indolo[2,3-b]quinoxaline (0.15 g, 0.37 mmol), bis-trimethylstannyl thiophene (0.73 g, 0.18 mmol), Silia*Cat*® DPP-Pd (0.05 g), and bench top toluene (4 mL) was added to a 5 mL microwave vial and sealed with a Teflon® cap. The vial was heated in a microwave reactor for at 150°C for 30 minutes. The reaction mixture was cooled to room temperature and poured into methanol (~300 mL). The orange solid was collected via suction filtration, dissolved in dichloromethane and solution filtered to remove the heterogeneous catalyst (Silia*Cat*® DPP-Pd). The solvent was removed under reduced pressure, the material slurried in methanol, and the resultant product was collected via suction filtration washing with ethanol and isopropanol. The collected solid was dried *in vacuo* yielding 0.21 g (77% yield) of compound **1**. ¹**H** NMR (300 MHz, CDCl₃, ppm): δ 0.86 (t, 6H), 1.21-1.36, (m, br, 12H), 1.36 – 1.55 (m, br, 8H), 1.96-2.03 (m, br, 4H), 4.52 (t, 4H), 7.53 (s, 2H), 7.62-7.75 (ov, 8H), 8.11 (dd, ${}^{1}J=$ 9.5 Hz, ${}^{2}J=$ 1.3 Hz, 2H), 8.27 (dd, ${}^{1}J=$ 9.5 Hz, ${}^{2}J=$ 1.2 Hz 2H), 8.46 (d, J= 8.0 Hz, 2H). ¹³C{¹H} NMR (300 MHz, CDCl₃, ppm): δ 14.1, 22.6, 27.1, 28.5, 29.2, 31.8, 41.5, 106.0, 118.7, 118.9, 123.2, 125.5, 126.0, 127.9, 128.7, 129.2, 136.6, 139.5, 140.6, 144.7, 144.9, 146.2.
Elemental Analysis: Calculated for C₄₈H₅₀N₆S: C, 77.6; H, 6.8; N, 11.3, Found: C, 76.4; H, 6.5; N, 11.1.

4.4 Synthesis of 8,8'-(4,8-bis(octan-3-yloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-octyl-6H-indolo[2,3-b]quinoxaline) (2).

8-bromo-indolo[2,3-b]quinoxaline (0.22 g, 0.53 mmol), 2,6-bis(trimethyltin)-4,8-bis(2ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene (0.19 g, 0.25 mmol), SiliaCat DPP-Pd (0.05 g), and bench top toluene (4 mL) was added to a 5 mL microwave vial and sealed with a Teflon® cap. The vial was heated in a microwave reactor at 150°C for 30 minutes. The reaction mixture was cooled to room temperature and poured into methanol (~300 mL). The dark orange solid was collected via filtration, dissolved in chloroform and solution filtered to remove the heterogeneous catalyst (Silia*Cat*® DPP-Pd). The solvent was removed under reduced pressure, the material slurried in methanol, and the resultant product was collected via suction filtration washing with ethanol and isopropanol. The collected solid was dried *in vacuo* yielding 0.17g (60 % yield) of compound **2**. ¹**H NMR** (300 MHz, 325 K, CDCl₃, ppm) δ 0.85 (t, 6H), 1.01 (t, 6H), 1.14 (t, 6H), 1.20 – 1.36 (m, br 12 H), 1.36-1.55 (m, br, 14 H), 1.55-2.10 (m, br, 16 H), 4.32 (d, J=5.4 Hz, 4H), 4.55 (t, 4H), 7.58 – 7.74 (m, 8H), 7.81 (s, 2H), 8.09 (d, *J*= 8.1 Hz, 2H), 8.25 (d, *J*= 8.0 Hz 2H), 8.47 (d, *J*= 8.1 Hz, 2H). ¹³C{¹H} NMR: Not able to obtain due to low solubility. **Elemental Analysis:** Calculated for C₇₀H₈₄N₆O₂S₂: C, 76.1; H, 7.7; N, 7.6. Found: C, 75.1; H, 7.4; N, 7.5.

4.5 Synthesis of 6,6'-di(thiophen-2-yl)-1,1'-di(octyl)isoindigo (Oct-II(Th)₂):

Synthesized according to literature procedure.[53]

4.6 Synthesis of 1,1'-dioctyl-6,6'-bis(5-(6-octyl-6H-indolo[2,3-b]quinoxalin-8-yl)thiophen-2-yl)-isoindigo (3):

A 5 mL pressure tube was loaded with Oct-II(Th)₂ (0.184 g, 0.283 mmol), IQ-Oct (0.253 g, 0.617 mmol), Pd(OAc)₂ (0.005 g, 8 mol%), pivalic acid (0.014g, 48 mol%), K₂CO₃ (0.100g, 0.724 mmol) and anhydrous DMF (4 mL). The reaction mixture was sealed under N₂ and heated at 100°C for 3 hours. Upon cooling to room temperature, the reaction mixture was poured into ~200 mL of a 1:1 H₂O:MeOH solution and left to stir for two hours. The fine black solid was isolated by suction filtration and washed with water, methanol, and ethanol. The product was further purified by flash column chromatography with chloroform as the eluent (55% yield). ¹H NMR (300 MHz, 325 K, CDCl₃, ppm) δ 0.87-0.97 (m, 14 H), 1.23-1.44 (m, 38H), 1.78 (t, 4 H), 1.97 (t, 4H), 3.84 (t, 4H), 4.46 (t, 4H), 6.79 (d, *J*= 1.4 Hz, 2H), 7.20 (dd, ^{*I*}*J*= 9.96 Hz, ²*J*= 1.5 Hz 2H), 7.34 (dd, ^{*I*}*J*= 14.2 Hz, ²*J*= 3.9 Hz 4H), 7.45 (s, 2H), 7.49 – 7.58 (m, 6H), 7.98 (dd, ^{*I*}*J*= 9.7 Hz, ²*J*= 2.1 Hz 2H), 8.18 (dd, ^{*I*}*J*= 9.8 Hz, ²*J*= 1.5 Hz 2H), 8.33 (d, *J*= 8.1 Hz, 2H), 9.13 (d, *J*= 8.4 Hz, 2H). ¹³C{¹H} NMR: Not able to obtain due to low solubility. Elemental Analysis: Calculated for C₈₄H₉₂N₈O₂S₂: C, 77.0; H, 7.1; N, 8.6. Found: C, 76.5; H, 7.0; N, 8.1.

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and computational details are available.

References

- [1] Li Y, Guo Q, Li Z, Pei J, Tian W. Solution processable D–A small molecules for bulkheterojunction solar cells. Energy Environ Sci 2010;3:1427–36. doi:10.1039/C003946B.
- [2] Würthner F, Meerholz K. Systems Chemistry Approach in Organic Photovoltaics. Chem -Eur J 2010;16:9366–73. doi:10.1002/chem.201001153.
- [3] Walker B, Kim C, Nguyen T-Q. Small Molecule Solution-Processed Bulk Heterojunction Solar Cells[†]. Chem Mater 2011;23:470–82. doi:10.1021/cm102189g.
- [4] Lin Y, Li Y, Zhan X. Small molecule semiconductors for high-efficiency organic photovoltaics. Chem Soc Rev 2012;41:4245–72. doi:10.1039/C2CS15313K.
- [5] Mishra A, Bäuerle P. Small Molecule Organic Semiconductors on the Move: Promises for Future Solar Energy Technology. Angew Chem Int Ed 2012;51:2020–67. doi:10.1002/anie.201102326.
- [6] Chen Y, Wan X, Long G. High Performance Photovoltaic Applications Using Solution-Processed Small Molecules. Acc Chem Res 2013;46:2645–55. doi:10.1021/ar400088c.
- [7] Roncali J, Leriche P, Blanchard P. Molecular Materials for Organic Photovoltaics: Small is Beautiful. Adv Mater 2014;26:3821–38. doi:10.1002/adma.201305999.
- [8] Kan B, Li M, Zhang Q, Liu F, Wan X, Wang Y, et al. A Series of Simple Oligomer-like Small Molecules Based on Oligothiophenes for Solution-Processed Solar Cells with High Efficiency. J Am Chem Soc 2015;137:3886–93. doi:10.1021/jacs.5b00305.
- [9] Ni W, Wan X, Li M, Wang Y, Chen Y. A–D–A small molecules for solution-processed organic photovoltaic cells. Chem Commun 2015;51:4936–50. doi:10.1039/C4CC09758K.
- [10] Mishra A, Fischer MKR, Bäuerle P. Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure: Property Relationships to Design Rules. Angew Chem Int Ed 2009;48:2474–99. doi:10.1002/anie.200804709.
- [11] Ooyama Y, Harima Y. Molecular Designs and Syntheses of Organic Dyes for Dye-Sensitized Solar Cells. Eur J Org Chem 2009;2009:2903–34. doi:10.1002/ejoc.200900236.
- [12] Yen Y-S, Chou H-H, Chen Y-C, Hsu C-Y, Lin JT. Recent developments in molecule-based organic materials for dye-sensitized solar cells. J Mater Chem 2012;22:8734–47. doi:10.1039/C2JM30362K.
- [13] Dessi A, Calamante M, Mordini A, Peruzzini M, Sinicropi A, Basosi R, et al. Organic dyes with intense light absorption especially suitable for application in thin-layer dye-sensitized solar cells. Chem Commun 2014;50:13952–5. doi:10.1039/C4CC06160H.
- [14] Allard S, Forster M, Souharce B, Thiem H, Scherf U. Organic Semiconductors for Solution-Processable Field-Effect Transistors (OFETs). Angew Chem Int Ed 2008;47:4070–98. doi:10.1002/anie.200701920.
- [15] Mas-Torrent M, Rovira C. Novel small molecules for organic field-effect transistors: towards processability and high performance. Chem Soc Rev 2008;37:827–38. doi:10.1039/B614393H.
- [16] Wang C, Dong H, Hu W, Liu Y, Zhu D. Semiconducting π-Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. Chem Rev 2012;112:2208– 67. doi:10.1021/cr100380z.

- [17] Mei J, Diao Y, Appleton AL, Fang L, Bao Z. Integrated Materials Design of Organic Semiconductors for Field-Effect Transistors. J Am Chem Soc 2013;135:6724–46. doi:10.1021/ja400881n.
- [18] Liu J, Wu Y, Qin C, Yang X, Yasuda T, Islam A, et al. A dopant-free hole-transporting material for efficient and stable perovskite solar cells. Energy Environ Sci 2014;7:2963–7. doi:10.1039/C4EE01589D.
- [19] Qin P, Paek S, Dar MI, Pellet N, Ko J, Grätzel M, et al. Perovskite Solar Cells with 12.8% Efficiency by Using Conjugated Quinolizino Acridine Based Hole Transporting Material. J Am Chem Soc 2014;136:8516–9. doi:10.1021/ja503272q.
- [20] Wang J, Wang S, Li X, Zhu L, Meng Q, Xiao Y, et al. Novel hole transporting materials with a linear π -conjugated structure for highly efficient perovskite solar cells. Chem Commun 2014;50:5829–32. doi:10.1039/C4CC01637H.
- [21] Ganesan P, Fu K, Gao P, Raabe I, Schenk K, Scopelliti R, et al. A simple spiro-type hole transporting material for efficient perovskite solar cells. Energy Environ Sci 2015. doi:10.1039/C4EE03773A.
- [22] Swetha T, Singh SP. Perovskite solar cells based on small molecule hole transporting materials. J Mater Chem A 2015. doi:10.1039/C5TA02507A.
- [23] Xu B, Tian H, Lin L, Qian D, Chen H, Zhang J, et al. Integrated Design of Organic Hole Transport Materials for Efficient Solid-State Dye-Sensitized Solar Cells. Adv Energy Mater 2015;5:n/a – n/a. doi:10.1002/aenm.201401185.
- [24] Darling SB, You F. The case for organic photovoltaics. RSC Adv 2013;3:17633–48. doi:10.1039/C3RA42989J.
- [25] Forrest SR. The path to ubiquitous and low-cost organic electronic appliances on plastic. Nature 2004;428:911–8. doi:10.1038/nature02498.
- [26] Kaltenbrunner M, White MS, Głowacki ED, Sekitani T, Someya T, Sariciftci NS, et al. Ultrathin and lightweight organic solar cells with high flexibility. Nat Commun 2012;3:770–7. doi:10.1038/ncomms1772.
- [27] Kippelen B, Brédas J-L. Organic photovoltaics. Energy Environ Sci 2009;2:251–61. doi:10.1039/B812502N.
- [28] Li G, Zhu R, Yang Y. Polymer solar cells. Nat Photonics 2012;6:153–61. doi:10.1038/nphoton.2012.11.
- [29] Søndergaard R, Hösel M, Angmo D, Larsen-Olsen TT, Krebs FC. Roll-to-roll fabrication of polymer solar cells. Mater Today 2012;15:36–49. doi:10.1016/S1369-7021(12)70019-6.
- [30] Su Y-W, Lan S-C, Wei K-H. Organic photovoltaics. Mater Today 2012;15:554–62. doi:10.1016/S1369-7021(13)70013-0.
- [31] McCulloch I. Organic Electronics. Adv Mater 2013;25:1811–2. doi:10.1002/adma,201205216.
- [32] Anthony JE. Organic electronics: Addressing challenges. Nat Mater 2014;13:773–5. doi:10.1038/nmat4034.
- [33] Irimia-Vladu M, Głowacki ED, Voss G, Bauer S, Sariciftci NS. Green and biodegradable electronics. Mater Today 2012;15:340–6. doi:10.1016/S1369-7021(12)70139-6.
- [34] Irimia-Vladu M. "Green" electronics: biodegradable and biocompatible materials and devices for sustainable future. Chem Soc Rev 2013;43:588–610. doi:10.1039/C3CS60235D.

- [35] Marzano G, Ciasca CV, Babudri F, Bianchi G, Pellegrino A, Po R, et al. Organometallic Approaches to Conjugated Polymers for Plastic Solar Cells: From Laboratory Synthesis to Industrial Production. Eur J Org Chem 2014;2014:6583–614. doi:10.1002/ejoc.201402226.
- [36] Osedach TP, Andrew TL, Bulović V. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. Energy Environ Sci 2013;6:711–8. doi:10.1039/C3EE24138F.
- [37] Roncali J, Thobie-Gautier C. An efficient strategy towards small bandgap polymers: The rigidification of the π -conjugated system. Adv Mater 1994;6:846–8. doi:10.1002/adma.19940061108.
- [38] Brisset H, Thobie-Gautier C, Gorgues A, Jubault M, Roncali J. Novel narrow bandgap polymers from sp3 carbon-bridged bithienyls: poly(4,4-ethylenedioxy-4H-cyclopenta[2,1-b;3,4-b']dithiophene). J Chem Soc Chem Commun 1994:1305–6. doi:10.1039/C39940001305.
- [39] Kitamura C, Tanaka S, Yamashita Y. Design of Narrow-Bandgap Polymers. Syntheses and Properties of Monomers and Polymers Containing Aromatic-Donor and o-Quinoid-Acceptor Units. Chem Mater 1996;8:570–8. doi:10.1021/cm950467m.
- [40] Brocks G, Tol A. Small Band Gap Semiconducting Polymers Made from Dye Molecules: Polysquaraines. J Phys Chem 1996;100:1838–46. doi:10.1021/jp952276c.
- [41] Yamamoto T, Zhou Z, Kanbara T, Shimura M, Kizu K, Maruyama T, et al. π -Conjugated Donor–Acceptor Copolymers Constituted of π -Excessive and π -Deficient Arylene Units. Optical and Electrochemical Properties in Relation to CT Structure of the Polymer. J Am Chem Soc 1996;118:10389–99. doi:10.1021/ja961550t.
- [42] Hari Narayana Moorthy NS, Karthikeyan C, Trivedi P. Design, synthesis, cytotoxic evaluation, and QSAR study of some 6H-indolo[2,3-b]quinoxaline derivatives. J Enzyme Inhib Med Chem 2010;25:394–405. doi:10.3109/14756360903190747.
- [43] Shibinskaya MO, Lyakhov SA, Mazepa AV, Andronati SA, Turov AV, Zholobak NM, et al. Synthesis, cytotoxicity, antiviral activity and interferon inducing ability of 6-(2aminoethyl)-6H-indolo[2,3-b]quinoxalines. Eur J Med Chem 2010;45:1237–43. doi:10.1016/j.ejmech.2009.12.014.
- [44] Narayana Moorthy NSH, Manivannan E, Karthikeyan C, Trivedi P. 6H-Indolo[2,3b]Quinoxalines: DNA and Protein Interacting Scaffold for Pharmacological Activities. Mini Rev Med Chem 2013;13:1415–20.
- [45] Thomas KRJ, Tyagi P. Synthesis, Spectra, and Theoretical Investigations of the Triarylamines Based on 6H-Indolo[2,3-b]quinoxaline. J Org Chem 2010;75:8100–11. doi:10.1021/jo1016663.
- [46] Tyagi P, Venkateswararao A, Thomas KRJ. Solution Processable Indoloquinoxaline Derivatives Containing Bulky Polyaromatic Hydrocarbons: Synthesis, Optical Spectra, and Electroluminescence. J Org Chem 2011;76:4571–81. doi:10.1021/jo2004764.
- [47] Venkateswararao A, Tyagi P, Justin Thomas KR, Chen P-W, Ho K-C. Organic dyes containing indolo[2,3-b]quinoxaline as a donor: synthesis, optical and photovoltaic properties. Tetrahedron 2014;70:6318–27. doi:10.1016/j.tet.2014.04.009.
- [48] Qian X, Gao H-H, Zhu Y-Z, Lu L, Zheng J-Y. 6H-Indolo[2,3-b]quinoxaline-based organic dyes containing different electron-rich conjugated linkers for highly efficient dye-sensitized solar cells. J Power Sources 2015;280:573–80. doi:10.1016/j.jpowsour.2015.01.148.

- [49] Przyjazna B, Kucybała Z, Pączkowski J. Development of new dyeing photoinitiators based on 6H-indolo[2,3-b]quinoxaline skeleton. Polymer 2004;45:2559–66. doi:10.1016/j.polymer.2004.02.025.
- [50] Dowlatabadi R, Khalaj A, Rahimian S, Montazeri M, Amini M, Shahverdi A, et al. Impact of Substituents on the Isatin Ring on the Reaction Between Isatins with Ortho-Phenylenediamine. Synth Commun 2011;41:1650–8. doi:10.1080/00397911.2010.491596.
- [51] Areephong J, Hendsbee AD, Welch GC. Facile synthesis of unsymmetrical and π-extended furan-diketopyrrolopyrrole derivatives through C–H direct (hetero)arylation using a heterogeneous catalyst system. New J Chem 2015. doi:10.1039/C5NJ01150G.
- [52] McAfee SM, McCahill JSJ, Macaulay CM, Hendsbee AD, Welch GC. Utility of a heterogeneous palladium catalyst for the synthesis of a molecular semiconductor via Stille, Suzuki, and direct heteroarylation cross-coupling reactions. RSC Adv 2015;5:26097–106. doi:10.1039/C5RA02468D.
- [53] McAfee SM, Topple JM, Payne A-J, Sun J-P, Hill IG, Welch GC. An Electron-Deficient Small Molecule Accessible from Sustainable Synthesis and Building Blocks for Use as a Fullerene Alternative in Organic Photovoltaics. ChemPhysChem 2015;16:1190–202. doi:10.1002/cphc.201402662.
- [54] Hendsbee AD, Macaulay CM, Welch GC. Synthesis of an H-aggregated thiophene– phthalimide based small molecule via microwave assisted direct arylation coupling reactions. Dyes Pigments 2014;102:204–9. doi:10.1016/j.dyepig.2013.10.046.
- [55] Sun J-P, Hendsbee AD, Eftaiha AF, Macaulay C, Rutledge LR, Welch GC, et al. Phthalimide–thiophene-based conjugated organic small molecules with high electron mobility. J Mater Chem C 2014;2:2612–21. doi:10.1039/C3TC32497D.
- [56] Hendsbee AD, Sun J-P, McCormick TM, Hill IG, Welch GC. Unusual loss of electron mobility upon furan for thiophene substitution in a molecular semiconductor. Org Electron 2015;18:118–25. doi:10.1016/j.orgel.2014.12.033.
- [57] Shen S, Jiang P, He C, Zhang J, Shen P, Zhang Y, et al. Solution-Processable Organic Molecule Photovoltaic Materials with Bithienyl-benzodithiophene Central Unit and Indenedione End Groups. Chem Mater 2013;25:2274–81. doi:10.1021/cm400782q.
- [58] Mei J, Graham KR, Stalder R, Reynolds JR. Synthesis of Isoindigo-Based Oligothiophenes for Molecular Bulk Heterojunction Solar Cells. Org Lett 2010;12:660–3. doi:10.1021/ol902512x.

Graphical Abstract:



Figures and Tables:





ACCEPTED MANUSCRIPT



Compound	Solution	Film	Film	Eopt	$HOMO^1$	$LUMO^{1}$	E_{g}
	λ_{onset} (nm)	λ_{onset}	λ_{max} (nm)	(eV)	(eV)	(eV)	(eV)
		(nm)					
1	492	545	440	2.28	-5.45	-3.51	1.94
2	525	565	405,440, 500	2.19	-5.28	-3.53	1.75
3	715	750	435,590	1.65	-5.31	-3.74	1.57

¹Determined using cyclic voltammetry









Figure 1. Organic π -conjugated indoloquinoxaline building block for use in organic electronics.

Figure 2. A) Literature preparation for indoloquinoxaline[42,49,50], B) incorporation of brominated indole under the same reaction conditions does not result in desired product IQ, C) modified literature procedure leads to desired product in high yields, and D) can be functionalized with desired alkyl side chain in quantitative yields.

Figure 3. Synthesis of three new small molecule chromophores 1-3. $R_1 = 2$ -ethylhexyl, $R_2 = n$ -octyl.

Table 1. Optical and Electrochemical Properties

Figure 4. Optical properties of small molecules 1-3 in CHCl₃. Absorption profiles in solution (dark solid lines) and as-cast spin coated films (dashed lines). Fluorescence profiles in solution (light solid lines).

Figure 5. Comparison of compounds **1**, **2**, and **3** to related materials previously described in the literature. R = 2-ethylpropyl, $R_1 = 2$ -ethylhexyl, $R_2 = n$ -Octyl. Tabulated data can be found in the supporting information.

Figure 6. Cyclic voltammograms of compounds 1-3 and their bandgaps estimated from comparison to ferrocene.

Figure 7. A) Optimized structure with truncated alkyl groups, B) electronic energy levels and molecular orbital descriptions, and C) predicted optical absorption spectra. Calculations carried out in gas-phase using DFT and TD-DFT methods at the B3LYP/6-31G(d,p) level of theory.

Highlights:

Introduction of a new indoloquinoxaline organic π -conjugated building block

Simple synthesis of functionalized indoloquinoxaline building blocks

Synthesis of three new chromophores with progressively red-shifted band gaps

CHR MAN

Indolequinoxaline as a Terminal Building Block for the Construction of π -Conjugated Small Molecules Relevant to Organic Electronics

Abby-Jo Payne, Jenny S. J. McCahill and Gregory C. Welch*

Department of Chemistry, Dalhousie University, 6274 Coburg Road, P.O. Box 15000, Halifax, Nova Scotia, Canada, B3H 4R2

> * Corresponding Author Email: gregory.welch@dal.ca Phone Number: 1 (902) 494 4245 Fax Number: 1 (902) 494 1310

SUPPORTING INFORMATION

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Materials and Methods Solution ¹H & ¹³C NMR Spectra Cyclic Voltammetry UV-Visible Absorption Spectra Reference Compound Comparison References

<u>1. Materials and Methods</u>

General Synthetic Details: Preparations were carried out on a bench top or under an atmosphere of dry, O_2 -free N_2 *via* Schlenk line techniques and/or an Innovative Technology Inc. N_2 atmosphere glove box. Purification by flash column chromatography was performed using a Biotage® Isolera flash system.

Materials: 1-bromooctane and pivalic acid (PivOH) were purchased from TCI America. Isoindigo starting materials 6-bromoisatin and 6-bromo-2-oxindole were acquired from Ontario Chemicals Inc. O-phenylenediamine was purchased from Alfa Aesar and 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene from LumeTech. Bis-trimethylstannyl thiophene, 2-tributylstannyl thiophene, magnesium sulphate, toluene (Tol), chloroform (CHCl₃), and o-xylene were purchased from Sigma-Aldrich. Tetrakis(triphenylphosphine) palladium(0) catalyst (Pd(PPh₃)₄) and SiliaCat® heterogeneous catalyst DPP-Pd were bought from Strem Chemicals and SiliCycle respectively. Anhydrous potassium carbonate was purchased from ACP chemicals, glacial acetic acid (AcOH) from Fisherbrand and anhydrous N,N'-dimethylformamide (DMF) from EMD Millipore. All other solvents were obtained from the Dalhousie solvent exchange program. All solvents and materials purchased were used without further purification.

Nuclear Magnetic Resonance (NMR): ¹H and ¹³C{¹H} (NMR) spectroscopy spectra were recorded on a Bruker Avance-300 MHz spectrometer at 300K unless otherwise specified. Chemical shifts are reported in parts per million (ppm) and are referenced to the external standard SiMe₄. Multiplicities are reported as: singlet (s), doublet (d), triplet (t), (dd) doublet of doublets, and multiplet (m).

Mass Spectrometry (MS): Mass spectrometry measurements were performed courtesy of Xiao Feng at the Dalhousie University Analytical Laboratory with a Bruker-Daltronics Micro TOF Mass Spectrometer. Atmospheric pressure chemical ionization (APCI) was used to ionize samples with a corona discharge voltage of 4000 V and a vaporizer temperature of 375 °C.

Elemental Analysis (EA): Elemental analysis measurements were performed courtesy of Patricia Granados at the Center for Environmental Analysis and Remediation at Saint Mary's University, Halifax, NS, B3H 3C3. Samples were run using a Perkin Elmer 2400 Series II CHN Analyzer.

Cyclic Voltammetry (CV): All electrochemical measurements were performed using a BASi epsilonTM EC in a standard three-electrode, one compartment configuration equipped with Ag wire, Pt wire and glassy carbon electrode, as the pseudo reference, counter electrode and working electrode respectively. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at scan rate 50 mV/s. All

electrochemical solutions were purged with dry N₂ for 5 minutes to deoxygenate the system. Solution CV measurements were carried out with a small molecule concentration of ~0.5 mg/mL in CH₂Cl₂. The HOMO and LUMO levels were obtained by correlating the onsets ($E_{ox}Fc/Fc+$, $E_{red}Fc/Fc+$) to the normal hydrogen electrode (NHE), assuming HOMO of Fc/Fc+ to be 4.88 eV.

UV-Visible Spectroscopy (UV-Vis): All absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis experiments were run in CHCl₃ using 10 mm quartz cuvettes. Neat films were prepared by spin-coating solutions from CHCl₃ onto glass substrates cut from Corning Micro slides (single frosted). Films were annealed by direct mounting on a VWR hotplate.

Photoluminescence (**PL**): All emission measurements were recorded using Agilent Technologies Cary Eclipse Fluorescence spectrophotometer at room temperature. All solution PL experiments were run in $CHCl_3$ using 10 mm quartz cuvettes.

Microwave-Assisted Synthesis: All microwave reactions were carried out using a Biotage® Initiator+ microwave reactor. The operational power range of the instrument is 0–400 W, using a 2.45 GHz magnetron. Pressurized air is used to cool each reaction after microwave heating.

Computational Details: To delve further into the nature of the geometric and electronic properties of **1-3**, gas-phase B3LYP/6-31G(d,p) ground-state equilibrium geometry optimizations were considered within Gaussian 09.¹ In order to reduce the computational cost while still accounting for the electron-donating ability of the substituent, the solubilizing chains along the conjugated backbone of **1-3** were truncated in all our calculations and represented as methyl groups. The dihedral angles that control the relative orientation of the π -systems were systematically altered for these three structures to help ensure that lower energy minima were not missed, where each resulting structure was characterized through frequency calculations at the same level of theory.

The low-lying singlet excited states of were also calculated using time-dependent density functional theory (TD-DFT) with B3LYP/6-31G(d,p) on the ground-state global minimum geometries. The absorption spectra were simulated through convolution of the vertical transition energies and oscillator strengths with Gaussian functions characterized by a full-width at half-maximum of 3000 cm⁻¹.

3. NMR Spectra



Figure S1. ¹H NMR spectra of IQ in DMSO-d₆.



Figure S2. ¹H NMR spectra of IQ-Oct in CDCl₃.



Figure S3. ¹H NMR spectra of 1 in CDCl₃.



Figure S4. ¹H NMR spectra of 2 in CDCl₃.



Figure S5. ¹H NMR spectra of 3 in CDCl₃.



Figure S6. Cyclic voltammetry plot of **1** obtained in CH_2Cl_2 solution, with oxidation onset = 0.57 V and reduction onset = -1.38 V.



Figure S7. Cyclic voltammetry plot of **2** obtained in CH_2Cl_2 solution, with oxidation onset = 0.40 V and reduction onset = -1.35 V.



Figure S8. Cyclic voltammetry plot of 3 obtained in CH_2Cl_2 solution, with oxidation onset = 0.43 V and reduction onset = -1.14 V.



Figure S9. UV-visible absorption spectra of **1** as a thin film cast from $CHCl_3$ on a glass substrate with subsequent thermal annealing for 5 minutes at each temperature.



Figure S10. UV-visible absorption spectra of **2** as a thin film cast from $CHCl_3$ on a glass substrate with subsequent thermal annealing for 5 minutes at each temperature.



Figure S11. UV-visible absorption spectra of **3** as a thin film cast from $CHCl_3$ on a glass substrate with subsequent thermal annealing for 5 minutes at each temperature.

Reference Compound Comparison



$R_1 = 2$ -ethylhexyl,	$R_2 =$	n-Oo	ctyl
		X	

Compound	Solution λonset (nm)	Film λonset (nm)	HOMO (eV)	LUMO (eV)	E _g (eV)
1	492	545	-5.5	-3.5	2.0
Phth-Th-Phth ^{2–4}	440	530	-6.5	-4.2*	2.3^{*}
2	525	565	-5.3	-3.5	1.8
DO1 ⁵	650	780	-5.2	-3.6	1.6
3	715	750	-5.3	-3.7	1.6
$II(Th_2)_2^6$	720	743	-5.6	-3.9	1.7
$Oct-II(ThPhth-1EP)_2^7$	675	720	-5.5	-3.6	1.9

* Energy levels obtained from UPS (all others estimated from CV)

References

- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Jr., J. A. M.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision C.01; Gaussian, Inc.: Wallingford CT, 2010.
- (2) Sun, J.-P.; Hendsbee, A. D.; Eftaiha, A. F.; Macaulay, C.; Rutledge, L. R.; Welch, G. C.; Hill, I. G. *J. Mater. Chem. C* **2014**, *2* (14), 2612–2621.
- (3) Hendsbee, A. D.; Macaulay, C. M.; Welch, G. C. *Dyes Pigments* **2014**, *102*, 204–209.
- (4) Hendsbee, A. D.; Sun, J.-P.; McCormick, T. M.; Hill, I. G.; Welch, G. C. *Org. Electron.* **2015**, *18*, 118–125.
- (5) Shen, S.; Jiang, P.; He, C.; Zhang, J.; Shen, P.; Zhang, Y.; Yi, Y.; Zhang, Z.; Li, Z.; Li, Y. Chem. Mater. 2013, 25 (11), 2274–2281.
- (6) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. Org. Lett. 2010, 12 (4), 660–663.
- (7) McAfee, S. M.; Topple, J. M.; Payne, A.-J.; Sun, J.-P.; Hill, I. G.; Welch, G. C. *ChemPhysChem* 2015, 16, 1190–1202.