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Synthesis of Aromatic Imide Tetramers Relevant to Organic Electronics by Direct (Hetero)Arylation

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SUPPORTING INFORMATION

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Materials and Methods

Materials: IDT core was purchased from Brilliant Matters. Silia*Cat*® DPP-Pd was received from SiliCycle. All remaining reagents were purchased from Sigma-Aldrich. Dimethyl acetamide solvent was dried by filtering through MgSO₄, stored over 3 Å molecular sieves, and purged with N_2 bubbling before use. All other solvents and materials purchased were used without further purification. Purification by flash column chromatography was performed using a Biotage® Isolera flash system.

Nuclear Magnetic Resonance (NMR): ¹H and ¹³C spectra were recorded on a Bruker Avance-500 MHz spectrometer at 300 K. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br).

High-resolution Mass Spectrometry (HRMS): High-resolution MALDI mass spectrometry measurements were performed courtesy of Jian Jun (Johnson) Li in the Chemical Instrumentation Facility at the University of Calgary. A Bruker Autoflex III Smartbeam MALDI-TOF (Na:YAG laser, 355nm), setting in positive or negative reflective mode, was used to acquire spectra. Operation settings were all typical, e.g. laser offset 62-69; laser frequency 200Hz; and number of shots 300. The target used was Bruker MTP 384 ground steel plate target. Sample solution (~ 1 μ g/mL in dichloromethane) was mixed with matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) solution (~ 5mg/mL in methanol). Pipetted 1 μ l solution above to target spot and dried in the fume hood.

CHN Analysis: Elemental analysis was performed by Jian Jun Li in the Chemical Instrumentation Facility at the University of Calgary. A Perkin Elmer 2400 Series II CHN Elemental Analyzer was used to obtain CHN data from a minimum of 3 mg of sample with particle sizes ranging between 0.2 and 0.5 mm in diameter. Results were obtained in duplicate.

Cyclic Voltammetry (CV): Electrochemical measurements were performed using a Model 1200B Series Handheld Potentiostat by CH Instruments Inc. The cyclic voltammetry experiments were performed in anhydrous solution with ~0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte using either dichloromethane solvent with Ag wire pseudo reference, Pt wire counter electrode, and glassy carbon electrode working electrode. All electrochemical solutions were purged with 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 dichloromethane. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the onsets ($E_{ox}Fc/Fc^+$, $E_{red}Fc/Fc^+$) to the normal hydrogen electrode (NHE), assuming the IP of Fc/Fc⁺ to be 4.80 eV.¹

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 of pure compounds were prepared by spin-coating ~0.2 mL from a 1 % wt/v CHCl₃ solution onto Corning glass micro slides. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

Photoluminescence (PL): All emission measurements were recorded using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature. Thin-films were prepared by spin-coating 1 wt/v% CHCl₃ solutions on Corning glass micro slides. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

Photoluminescence Quantum Yield Determination: The photoluminescence quantum yield (PL QY) of compounds were estimated by using the comparative method proposed by Williams *et. al.*² after slight modification as follows:

$$Q_x = Q_R \frac{A_R}{A_X} \frac{F_X}{F_R} \left(\frac{\eta_X}{\eta_R}\right)^2$$

where *Q* is the PL QY, *A* is the absorbance of the solution, *F* is the corrected PL emission intensity, and η is the refractive index of the solution. Subscripts *R* and *X* refer to the standard and sample compounds, respectively. Rhodamine B³ (QY 0.7) was used as the standard for (PDI)₄ThTh and (Naphth)₄IDT. Rhodamine 6G³ (QY 0.95) was used as the standard for (Phth)₄IDT. Quinine sulfate³ (QY 0.546) (Sigma-Aldrich Co., St Louis, MO, USA) was used as the standard for (Phth)₄ThTh and (Naphth)₄ThTh. To minimize reabsorption effects, the absorbance maxima values of the standard and sample solutions were controlled to be less than 0.1. An excitation wavelength of 510 nm was chosen for rhodamine B, (PDI)₄ThTh, and (Naphth)₄IDT; 480 nm for rhodamine 6G and (Phth)₄IDT; and 347 nm for quinine sulfate, (Phth)₄ThTh, and (Naphth)₄ThTh. Absorption and PL spectra were recorded in methanol for rhodamine B; ethanol for rhodamine 6G, 0.5 M aqueous H₂SO₄ for quinine sulfate, chlorobenzene for (Phth)₄IDT. Refractive indices for methanol, ethanol, 0.5 M H₂SO₄, chlorobenzene, and chloroform are 1.3145, 1.361, 1.346, 1.5421, and 1.4382 respectively. Each QY was measured in triplicate.

Experimental

The *N*-annulated perylene diimide, *N*-hexyl phthalimide, and *N*-hexyl naphthalimide building blocks were synthesized according to our previously reported literature procedures.^{4–6}

Synthesis of (Phth)4IDT, 1a



In a 5 mL pressure vial, indacenodithieno[3,2-*b*]thiophene (50 mg, 0.049 mmol, 1.0 eq), 4-bromo-1-(hexyl)phthalimide (81 mg, 0.26 mmol, 5.4 eq), Silia*Cat*® DPP-Pd (34 mol% Pd to IDT), pivalic acid (96 mol% to IDT), and potassium carbonate (42 mg, 0.30 mmol, 6.2 eq.) were added with a stir bar followed by the addition of anhydrous, degassed *N*,*N*'-dimethylacetamide (1 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 120 °C in a LabArmor® bead bath for 24 hours. After 24 hours, the reaction mixture was poured into EtOH (50 mL) and stirred overnight. The mixture was filtered through celite, rinsing with EtOH to remove an orange solution. A yellow orange solid was recovered from the celite by washing with CH₂Cl₂. The CH₂Cl₂ was removed by rotary evaporation and the solid was isolated by precipitation with H₂O and vacuum filtration, rinsing with H₂O/MeOH. Pure product was isolated without any further purification as a yellow orange powder (24 mg, 0.012 mmol, 25% yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 7.89 (m, 2H, Phth aryl), 7.84 (d, 2H, *J*=7.7 Hz, Phth aryl), 7.74 (m, 2H, Phth aryl), 7.73, (dd, 2H, *J*=7.6, 1.7 Hz, Phth aryl), 7.67 (d, 2H, *J*=7.6 Hz, Phth aryl), 7.54 (s, 2H, IDT aryl), 7.50, (dd, 2H, *J*=7.6, 1.7 Hz, Phth aryl), 7.20, (d, 4H, *J*=8.3 Hz, IDT aryl), 7.13 (d, 4H, *J*=8.3 Hz, IDT aryl) 3.66 (m, 8H, N-CH₂), 2.57 (m, 8H, Ar-CH₂), 1.70-1.56 (m, 16H, CH₂), 1.32-1.25 (m, 48H, CH₂), 0.90-0.85 (m, 24H, CH₃).

¹³**C NMR** (151 MHz, CDCl₃, ppm): δ 168.0, 167.9, 167.9, 153.8, 146.8, 144.0, 143.6, 142.3, 140.5, 140.0, 139.9, 138.6, 136.2, 134.6, 134.3, 133.5, 133.2, 133.2, 131.7, 131.2, 130.9, 128.8, 128.0, 124.2, 123.7, 123.7, 123.5, 117.5, 63.4, 38.5, 38.4, 35.8, 31.8, 31.5, 31.5, 31.4, 29.3, 28.7, 28.7, 26.7, 26.7, 22.7, 22.7, 22.7, 14.3, 14.2, 14.2. Tabulated aromatic peaks: 28; Tabulated aliphatic peaks: 19

MS (MALDI-TOF): Calculated: 1934.9079; Found: 1934.9088

Elemental Analysis (EA): Theoretical: C= 76.90%, H= 6.97%, N= 2.89%; Found: C= 74.87%, H= 6.71%, N= 2.83%

Synthesis of (Naphth)4IDT, 1b



In a 5 mL pressure vial, indacenodithieno[3,2-*b*]thiophene (49 mg, 0.048 mmol, 1.0 eq), 4-bromo-1-(hexyl)naphthalimide (89 mg, 0.25 mmol, 5.2 eq), Silia*Cat*® DPP-Pd (33 mol % Pd to IDT), pivalic acid (61 mol% to IDT), and potassium carbonate (45 mg, 0.32 mmol, 6.7 eq.) were added with a stir bar followed by the addition of anhydrous, degassed *N*,*N*'-dimethylacetamide (1 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 120 °C in a LabArmor® bead bath for 24 hours. After 24 hours, the reaction mixture was poured into MeOH (50 mL) and stirred overnight. The mixture was filtered through celite, rinsing with MeOH to remove an orange brown solution. A red orange solid was recovered from the celite by washing with CH₂Cl₂. The CH₂Cl₂ was removed by rotary evaporation and the solid was isolated by precipitation with MeOH and vacuum filtration. The solid product was suspended in acetone (20 mL) and stirred at reflux for 30 minutes. The resulting solution was allowed to cool to room temperature and then cooled at -30 °C overnight. The resulting material was subsequently isolated by vacuum filtration washing with acetone to yield the desired product as a red orange powder (17 mg, 0.0079 mmol, 16% yield).

¹**H** NMR (500 MHz, CDCl₃, ppm): δ 8.56 (d, br, 2H, *J*=7.7 Hz, Naphth aryl), 8.42 (d, 2H, *J*=7.7 Hz, Naphth aryl), 8.39 (d, 2H, *J*=7.7 Hz, Naphth aryl), 8.34, (dd, 4H, *J*=7.6, 1.7 Hz, Naphth aryl), 8.29 (d, 2H, *J*=7.6 Hz, Naphth aryl), 7.69 (d, 2H, Naphth aryl), 7.62, (m, 2H, Naphth aryl), 7.56 (d, 2H, *J*=7.7 Hz, Naphth aryl), 7.50 (s, 2H, IDT aryl), 7.38 (dd, 2H, *J*=7.7 Hz, Naphth aryl), 7.22 (m, 8H, IDT aryl), 7.15 (m, 8H, IDT aryl), 4.10 (m, 8H, N-CH₂), 2.58 (m, 8H, Ar-CH₂), 1.71-1.53 (m, 16H, CH₂), 1.41-1.20 (m, 48H, CH₂), 0.87 (m, 24H, CH₃).

¹³**C NMR** (151 MHz, CDCl₃, ppm): δ 164.0, 163.9, 163.8, 163.7, 153.7, 146.4, 144.1, 143.8, 142.4, 140.2, 140.2, 140.0, 138.6, 138.0, 137.9, 136.2, 134.0, 132.0, 131.6, 131.5, 130.7, 130.5, 130.2, 129.4, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 127.2, 127.1, 123.4 123.1, 122.9, 122.8, 117.5, 63.5, 40.7, 35.8, 31.9, 31.8, 31.7, 31.7, 31.5, 31.4, 31.4, 29.3, 29.3, 28.2, 28.1, 26.9, 22.8, 22.7, 22.7, 22.7, 22.7, 14.3, 14.2, 14.2, 14.2, 14.2, 14.2.

Tabulated aromatic peaks: 38; Tabulated aliphatic peaks: 27

MS (MALDI-TOF): Calculated: 2134.9705; Found: 2134.9672

Elemental Analysis (EA): Theoretical: C= 78.69%, H= 6.70%, N= 2.62%; Found: C= 77.08%, H= 6.38%, N= 2.54%

Synthesis of (Phth)₄ThTh, 2a



In a 5 mL pressure vial, thieno[3,2-*b*]thiophene (30.0 mg, 0.21 mmol, 1.0 eq), 4-bromo-1-(hexyl)phthalimide (296 mg, 0.95 mmol, 4.5 eq), Silia*Cat*® DPP-Pd (10 mol% Pd to ThTh), pivalic acid (32 mol% to ThTh), and potassium carbonate (133 mg, 0.97 mmol, 4.5 eq.) were added with a stir bar followed by the addition of anhydrous, degassed *N*,*N*'-dimethylacetamide (3.3 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 120 °C in a LabArmor® bead bath for 24 hours. After 24 hours, the reaction mixture was poured into MeOH (50 mL) and stirred for 1 hour. The mixture was filtered through celite, rinsing with MeOH to remove a yellow filtrate. An orange solid was recovered from the celite by washing with CH₂Cl₂. The CH₂Cl₂ was removed by rotary evaporation and the solid was isolated by precipitation with MeOH and vacuum filtration. The solid was purified *via* column chromatography eluting with a CH₂Cl₂ to EtOAc gradient. Pure product was isolated with 4% EtOAc as a yellow powder (32 mg, 0.030 mmol, 14% yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 7.91 (m, 2H, aryl), 7.89 (d, 2H, *J*=7.7 Hz, aryl), 7.77 (m, 6H, aryl), 7.62, (dd, 2H, *J*=7.6, 1.7 Hz, aryl), 3.68 (m, 8H, N-CH₂), 1.67 (m, 8H, CH₂), 1.38-1.25 (m, 24H, CH₂), 0.89 (t, 6H, *J*=6.9 Hz, CH₃), 0.88 (t, 6H, *J*=7.0 Hz, CH₃).

¹³C NMR (151 MHz, CDCl₃, ppm): δ 167.8, 167.8, 167.7, 167.7, 140.2, 139.9, 139.8, 139.2, 134.7, 134.5, 133.7, 133.4, 132.0, 131.8, 130.6, 124.4, 124.0, 123.8, 123.5, 38.5, 38.5, 31.5, 31.5, 28.7, 28.7, 26.7, 26.7, 22.7, 22.7, 14.2, 14.2.

Tabulated aromatic peaks: 19; Tabulated aliphatic peaks: 12

MS (MALDI-TOF): Calculated: 1056.417; Found: 1056.746

Elemental Analysis (EA): Theoretical: C= 70.43%, H= 6.10%, N= 5.30%; Found: C= 70.44%, H= 6.23%, N= 5.15%

Synthesis of (Naphth)₄ThTh, 2b



In a 5 mL pressure vial, thieno[3,2-*b*]thiophene (30 mg, 0.22 mmol, 1.0 eq), 4-bromo-1-(hexyl)naphthalimide (341 mg, 0.95 mmol, 4.4 eq), Pd(OAc)₂ (30 mol% Pd to ThTh), pivalic acid (34 mol% to ThTh), and potassium carbonate (137 mg, 0.99 mmol, 4.6 eq.) were added with a stir bar followed by the addition of anhydrous, degassed N,N'-dimethylacetamide (3.5 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 120 °C in a LabArmor® bead bath for 24 hours. After 24 hours, the reaction mixture was poured into MeOH (50 mL) and stirred for 1 hour. The mixture was filtered through celite, rinsing with MeOH to remove a brown filtrate. A brown solid was recovered from the celite by washing with CH₂Cl₂. The CH₂Cl₂ was removed by rotary evaporation and the solid was isolated by precipitation with MeOH and vacuum filtration. The solid product was dissolved in CH₂Cl₂ and purified with a silica plug by eluting with pure CH₂Cl₂ to remove impurities, then eluting with a 5:95 by volume EtOAc:CH₂Cl₂ solvent mixture to yield the desired product as an orange powder (113 mg, 0.090 mmol, 42% yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 8.60 (dd, 1H, *J*=7.3, 1.0 Hz, aryl), 8.56 (dd, 1H, *J*=7.3, 1.0 Hz, aryl), 8.52-8.46 (m, 4H, aryl), 8.42-8.38 (m, 4H, aryl), 7.79 (d, 1H, *J*=7.6 Hz, aryl), 7.75-7.71 (m, 3H, aryl), 7.66 (d, 1H, *J*=7.6 Hz, aryl), 7.65, (dd, 1H, *J*=8.4, 7.4 Hz, aryl) 7.51 (dd, 2H, *J*=8.1, 8.1 Hz, aryl), 4.11 (m, 8H, N-CH₂), 1.66 (m, 8H, CH₂), 1.42-1.25 (m, 24H, CH₂), 0.87 (m, 6H, CH₃), 0.86 (m, 6H, CH₃).

¹³**C NMR** (151 MHz, CDCl₃, ppm): δ 163.9, 163.8, 163.8, 163.7, 163.6, 163.6, 141.5, 141.4, 139.8, 139.6, 137.9, 137.9, 137.0, 131.8, 131.6, 131.6, 131.5, 131.5, 131.5, 131.5, 131.4, 130.8, 130.7, 130.6, 130.4, 130.3, 130.2, 130.1, 129.5, 129.2, 129.0, 128.8, 128.8, 128.5, 127.5, 127.5, 123.7, 123.6, 123.5, 123.5, 123.4, 123.3, 123.3, 40.8, 31.7, 31.6, 28.2, 28.1, 26.9, 26.9, 22.7, 22.7, 14.2, 14.2.

Tabulated aromatic peaks: 45; Tabulated aliphatic peaks: 11

MS (MALDI-TOF): Calculated: 1256.480; Found: 1256.921

Elemental Analysis (EA): Theoretical: C= 74.50%, H= 5.77%, N= 4.46%; Found: C= 73.98%, H= 5.89%, N= 4.40%

Synthesis of (PDI)₄ThTh, 2c



In a 5 mL pressure vial, thieno[3,2-*b*]thiophene (15 mg, 0.11 mmol, 1.0 eq), 11-bromo-5-hexyl-2,8-bis(1-ethyl-propyl)perylene diimide (337 mg, 0.48 mmol, 4.5 eq), Silia*Cat*® DPP-Pd (10 mol% Pd to ThTh), pivalic acid (45 mol% to ThTh), and potassium carbonate (70 mg, 0.51 mmol, 4.7 eq.) were added with a stir bar followed by the addition of anhydrous, degassed *N*,*N*'-dimethylacetamide (3 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 120 °C in a LabArmor® bead bath for 24 hours. After 24 hours, the reaction mixture was poured into MeOH (50 mL) and stirred for 1.5 hours. The mixture was filtered through celite, rinsing with MeOH to remove a dark blue filtrate. A red solid was recovered from the celite by washing with CH₂Cl₂. The CH₂Cl₂ was removed by rotary evaporation and the solid was isolated by precipitation with MeOH and vacuum filtration. The solid was allowed to cool to room temperature and the resulting material was subsequently isolated by vacuum filtration washing with EtOAc to yield the desired product as a dark red powder (142 mg, 0.054 mmol, 50% yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 9.28 (s, br, 2H, aryl), 9.04 (s, br, 2H, aryl), 8.94 (s, br, 2H, aryl), 8.86 (s, br, 4H, aryl), 8.80 (s, br, 2H, aryl), 8.79 (s, br, 2H, aryl), 8.69 (s, br, 2H, aryl), 8.56 (m, 2H, aryl), 5.23 (m, 4H, N-CH), 4.83 (m, 12H, N-CH/N-CH₂), 2.52-2.26 (m, br, 8H, CH₂), 2.23-1.88 (m, 24H, CH₂), 1.85-1.67 (m, 8H, CH₂), 1.63 (m, 4H, CH₂), 1.45-1.16 (m, 20H), 1.11-0.39 (m, 60H, CH₃).

¹³C NMR (151 MHz, CDCl₃, ppm): δ 167.8, 167.8, 167.7, 167.7, 140.2, 139.9, 139.8, 139.2, 134.7, 134.5, 133.7, 133.4, 132.0, 131.8, 130.6, 124.4, 124.0, 123.8, 123.5, 38.5, 38.5, 31.5, 31.5, 28.7, 28.7, 26.7, 26.7, 22.7, 22.7, 14.2, 14.2.

Tabulated aromatic peaks: 19; Tabulated aliphatic peaks: 12

MS (MALDI-TOF): Calculated: 2641.152; Found: 2641.924

Elemental Analysis (EA): Theoretical: C= 75.13%, H= 6.10%, N= 6.36%; Found: C= 74.05%, H= 6.14%, N= 6.14%





Figure S1: ¹H NMR spectrum of (Phth)₄IDT in CDCl₃.



Figure S2: ¹³C NMR spectrum of (Phth)₄IDT in CDCl₃.



Figure S3: ¹H NMR spectrum of (Naphth)₄IDT in CDCl₃.



Figure S4: ¹H NMR spectrum of the aromatic region for (Naphth)₄IDT in CDCl₃.





Figure S6: ¹³C NMR spectrum of the aromatic region for (Naphth)₄IDT in CDCl₃.



Figure S7: ¹H NMR spectrum of (Phth)₄ThTh in CDCl₃.



Figure S8: ¹³C NMR spectrum of (Phth)₄ThTh in CDCl₃.



Figure S9: ¹H NMR spectrum of (Naphth)₄ThTh in CDCl₃.



Figure S10: ¹H NMR spectrum of the aromatic region for (Naphth)₄ThTh in CDCl₃.



Figure S11: ¹H NMR spectra of the aromatic region for $(Naphth)_4$ ThTh at different temperatures, measured in C₂D₂Cl₄.



Figure S12: ¹³C NMR spectrum of (Naphth)₄ThTh in CDCl₃.



Figure S13: ¹³C NMR spectrum of the aromatic region for (Naphth)₄ThTh in CDCl₃.



Figure S14: ¹H NMR spectrum of (PDI)₄ThTh in CDCl₃.



Figure S15: ¹H NMR spectra of the aromatic region for (PDI)₄ThTh at different temperatures, measured in $C_2D_2Cl_4$.



Figure S16: ¹³C NMR spectrum of (PDI)₄ThTh in CDCl₃.

Mass Spectra (MALDI-TOF)



Figure S17: MALDI-TOF of (Phth)₄IDT.







Figure S19: MALDI-TOF of (Phth)₄ThTh.



Figure S20: MALDI-TOF of (Naphth)₄ThTh.



Figure S21: MALDI-TOF of (PDI)₄ThTh.



Figure S22: MALDI-TOF of unpurified (Phth)₄ThTh showing lower substitution byproducts.



Figure S23: MALDI-TOF of unpurified (Naphth)₄ThTh showing lower substitution byproducts.



Figure S24: MALDI-TOF of unpurified (PDI)₄ThTh showing lower substitution byproducts.

Elemental Analysis

University of Calgary Department of Chemistry		EA Date: 2/6/2019		University Departmer	EA Date: 1/23/2019			
Name:	том	Group: GW		Name:	TOM	Group:	GW	
Sample:	TAW330-1	Weight (mg):	0.99	Sample:	TAW330-2	Weight (m	g):	1.202
%C (Actual):	74.83	%C (Theorectical):	76.90	%C (Actual):	74.87	%C (Theor	ectical):	76.90
%H (Actual):	6.71	%H (Theoretical):	6.97	%H (Actual):	6.71	%H (Theor	etical):	6.97
%N (Actual):	2.84	%N (Theoretical):	2.89	%N (Actual):	2.83	%N (Theor	etical):	2.89

Figure S25: Elemental analysis results for (Phth)₄IDT (low %C due to incomplete combustion).

University of Calgary Department of Chemistry		EA Date	e: 1/23/2	1/23/2019		University of Calgary Department of Chemistry			EA Date:		1/23/2019		
Name:	том	Group:	GW			Name:	TOM		Group:	GW			
Sample:	TAW331-1	Weight (mg):	1.226			Sample:	TAW33	1-2	Weight (m	g):	1.782		
%C (Actual):	77.02	%C (Theorectic	al):	78.69		%C (Actual):		77.08	%C (Theor	ectical):	78	3.69	
%H (Actual):	6.39	%H (Theoretica	al):	6.70		%H (Actual):		6.38	%H (Theor	etical):	6	5.70	
%N (Actual):	2.55	%N (Theoretica	al):	2.62		%N (Actual):		2.54	%N (Theo	retical):		2.62	1

Figure S26: Elemental analysis results for (Naphth)₄IDT (low %C due to incomplete combustion).

University of Calgary Department of Chemistry			τγ ΕΑ	ate:	9/20/2018	University Departmer	EA	ate:	9/20/2018	
	Name:	TOM	Group:	GW		Name:	ТОМ	Group:	GW	
	Sample:	PHTH4-1	Weight (mg		1.21	Sample:	PHTH4-2	Weight (mg		0.991
	%C (Actual):	70.44	%C (Theore	tical):	70.43	%C (Actual):	70.51	%C (Theore	tical):	70.43
	%H (Actual):	6.23	%H (Theore	ical):	6.10	%H (Actual):	6.22	%H (Theor∈	cal):	6.10
	%N (Actual):	5.15	%N (Theore	ical):	5.30	%N (Actual):	5.19	%N (Theore	ical):	5.30

Figure S27: Elemental analysis results for (Phth)₄ThTh.

University Departme	of Calgary nt of Chemistry	EA ate:	9/20/2018	University Departmer	of Calgary nt of Chemistry	EA	ate:	9/20/2018
Name:	TOM	Group: GW		Name:	том	Group:	GW	
Sample:	NAPHTH4-1	Weight (mg	1.132	Sample:	NAPHTH4-2	Weight (mg		1.32
%C (Actual):	73.98	%C (Theore tical):	74.50	%C (Actual):	73.95	%C (Theore	tical):	74.50
%H (Actual):	5.89	%H (Theore ical):	5.77	%H (Actual):	5.85	%H (Theore	ical):	5.77
%N (Actual):	4.40	%N (Theore ical):	4.46	%N (Actual):	4.44	%N (Theore	cal):	4.46

Figure S28: Elemental analysis results for (Naphth)₄ThTh.

_	University Departmer	of Calg nt of Ch	ary nemistry	EA	ate:	9/20/2018		University Departmer	of Calg nt of Ch	ary iemistry	EA)ate:	9/20/201	8
	Name:	ТОМ		Group:	GW			Name:	TOM		Group:	GW		
	Sample:	PDI4-1		Weight (mg		1.331		Sample:	PDI4-2		Weight (m	g :	1.372	
	%C (Actual):		74.05	%C (Theore	tical):	75.	43	%C (Actual):		74.31	%C (Theore	e tical):	7	5.43
	%H (Actual):		6.13	%H (Theore	ical):	6.	.10	%H (Actual):		6.21	%H (Theor	e idal):		6.10
	%N (Actual):		6.14	%N (Theore	ical):	6	5.36	%N (Actual):		6.11	%N (Theor	e ical):		6.36

Figure S29: Elemental analysis results for (PDI)₄ThTh.

Differential Scanning Calorimetry



Figure S30: DSC profile for (Phth)₄ThTh.



Figure S31: DSC profile for (Naphth)₄ThTh.



Figure S32: DSC profile for (PDI)₄ThTh.



Optoelectronic Characterization (Cyclic Voltammetry/UV-Vis)

Figure S33: Cyclic voltammogram of (Phth)₄IDT measured at 100 mV/s in CH₂Cl₂.

Figure S34: Differential pulse voltammogram of (Phth)₄IDT measured in CH₂Cl₂.

Figure S35: Cyclic voltammogram of (Naphth)₄IDT measured at 100 mV/s in CH₂Cl₂.

Figure S36: Differential pulse voltammogram of (Naphth)₄IDT measured in CH₂Cl₂.

Figure S37: Cyclic voltammogram of (PDI)₄IDT measured at 100 mV/s in CH₂Cl₂.

Figure S38: Cyclic voltammogram of (Phth)₄ThTh measured at 100 mV/s in CH₂Cl₂.

Figure S39: Differential pulse voltammogram of (Phth)₄ThTh measured in CH₂Cl₂.

Figure S40: Cyclic voltammogram of (Naphth)₄ThTh measured at 100 mV/s in CH₂Cl₂.

Figure S41: Differential pulse voltammogram of (Naphth)₄ThTh measured in CH₂Cl₂.

Figure S42: Cyclic voltammogram of (PDI)₄ThTh measured at 100 mV/s in CH₂Cl₂.

Figure S43: Differential pulse voltammogram of (PDI)₄ThTh measured in CH₂Cl₂.⁷

Figure S44: Solution absorption spectra for (Phth)₄IDT in CHCl₃.

Figure S45: Absorbance versus concentration profile for (Phth)₄IDT.

Figure S46: CHCl₃ solution absorption and emission spectra for (Phth)₄IDT.

Figure S47: Thin film absorption and emission spectra for (Phth)₄IDT.

Figure S48: Solution absorption spectra for (Naphth)₄IDT in CHCl₃.

Figure S49: Absorbance versus concentration profile for (Naphth)₄IDT.

Figure S50: CHCl₃ solution absorption and emission spectra for (Naphth)₄IDT.

Figure S51: Thin film absorption and emission spectra for (Naphth)₄IDT.

Figure S52: CHCl₃ solution absorption and emission spectra for (PDI)₄IDT.⁷

Figure S53: Thin film absorption and emission spectra for (PDI)₄IDT.⁷

Figure S54: Solution absorption spectra for (Phth)₄ThTh in CHCl₃.

Figure S55: Absorbance versus concentration profile for (Phth)₄ThTh.

Figure S56: CHCl₃ solution absorption and emission spectra for (Phth)₄ThTh.

Figure S57: Thin film absorption and emission spectra for (Phth)₄ThTh.

Figure S58: Solution absorption spectra for (Naphth)₄ThTh in CHCl₃.

Figure S59: Absorbance versus concentration profile for (Naphth)₄ThTh.

Figure S60: CHCl₃ solution absorption and emission spectra for (Naphth)₄ThTh.

Figure S61: Thin film absorption and emission spectra for (Naphth)₄ThTh.

Figure S62: Solution absorption spectra for (PDI)₄ThTh in CHCl₃.

Figure S63: Absorbance versus concentration profile for (PDI)₄ThTh.

Figure S64: CHCl₃ solution absorption and emission spectra for (PDI)₄ThTh.

Figure S65: Thin film absorption and emission spectra for (PDI)₄ThTh.

	(Phth) ₄ IDT	(Naphth)4IDT	(PDI) ₄ IDT ⁷	(Phth) ₄ ThTh	(Naphth) ₄ ThTh	(PDI) ₄ ThTh
Ox E _{on} (V)	0.50	0.56	0.57	NA	NA	1.03
Ox $E_{1/2}$ (V)	0.60, 0.96	0.63, 0.95	0.62, 1.03	NA	NA	1.13
Red E _{on} (V)	-1.79	-1.66	-1.16	-1.73	-1.63	-1.19
Red $E_{1/2}(V)$	-1.92, -2.00	-1.74	-1.43, -1.57	-1.86, -1.99	-1.72	-1.28, -1.38, -1.55, -1.69
IP $(eV)^a$	5.3	5.3	5.3	NA	NA	5.8
EA $(eV)^a$	3.0	3.1	3.6	3.1	3.2	3.6
Eg	2.3	2.2	1.7	NA	NA	2.2
Abs λ _{max}	467	470, 400, 350	533, 498, 424	388, 344	350	532, 496
Em λ _{max} (nm)	583	608	748	474	496	604
Stokes Shift (eV) ^b	0.53	0.60	0.67	0.57	1.04	0.28
ε λ _{max} (L mol ⁻¹ cm ⁻¹)	40 670	52 440	209 800	24 070	58 430	119 250
Integrated ε (10 ⁵)	55.8	83.0	228.8	26.4	50.3	133.5
Quantum Vield (%)	14	21	<1	13	6	34

 $\mathbf{Y} = \mathbf{I} =$

^{*a*}Energies were calculated by (Eon+4.8) where Fc HOMO = 4.8 eV.¹

^bStokes Shifts were calculated by $(E_{\lambda abs} - E_{\lambda ems})$ where $(E_{\lambda max} = h^*c/\lambda_{max}; h = Planck's Constant, c = speed of light)$.

Figure S66: Cyclic voltammogram of $(Naphth)_4$ ThTh reduction at different scan rates in CH₂Cl₂. By applying the Randles-Sevcik equation,⁸ it is found that peak current for reduction at -1.7 V is proportional to the square root of the scan rate, indicating a diffusion dependent process. Oxidation peak current at -0.9 V is proportional to the scan rate directly, indicating an adsorption dependent process.⁹ See Figures S67 to S70, below.

Figure S67: Reduction peak potential versus sqrt scan rate of (Naphth)₄ThTh.

Figure S68: Reduction peak potential versus scan rate of (Naphth)₄ThTh.

Figure S69: Reverse reduction peak potential versus sqrt scan rate of (Naphth)₄ThTh.

Figure S70: Reverse reduction peak potential versus scan rate of (Naphth)₄ThTh.

Figure S71: Normalized absorbance profiles for the individual tetramer components, measured in CHCl_{3.}

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