Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Pyridine-Terminated Low Gap π-Conjugated Oligomers: Design, Synthesis, and Photophysical Response to Protonation and Metalation

Asmerom O. Weldeab, Lei Li, Seda Cekli, Khalil A. Abboud, Kirk S. Schanze, and Ronald K. Castellano

General Methods

Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. THF and DMF were degassed in 20 L drums and passed through two sequential purification columns (activated alumina; molecular sieves for DMF) under a positive argon atmosphere. Thin layer chromatography (TLC) was performed on SiO_2-60 F_{254} aluminum plates with visualization by UV light or staining. Flash column chromatography was performed using silica gel technical grade, pore size 60 Å, 230−400 mesh particle size, 40−63 µm particle size from Sigma-Aldrich. ^1H (^{13}C) NMR were recorded on Mercury 300 or INOVA 500 spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS and referenced to residual protonated solvent purchased from Cambridge Isotope Laboratories, Inc. ($CDCl_3$: δH 7.26 ppm, δC 77.16 ppm; DMSO-d_6: δH 2.50 ppm, δC 39.52 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), hp (heptet), b (broad), and m (multiplet). Electrospray ionization (ESI) high resolution mass spectra (HRMS) were recorded on an Agilent 6210 TOF spectrometer with MassHunter software. Absorption spectra were recorded on a UV-Vis-near-IR spectrophotometer. Emission spectra were recorded on a Photon Technology International (PTI) fluorimeter and collected 90° relative to the excitation beam. Ground state geometries and orbital energies of the molecules in the gas phase were obtained from DFT calculations at the B3LYP/6-31G* level as implemented in Gaussian 09,[1] accessed through UF Research Computing. Frequency calculations were performed to confirm the final geometries as energy minima. Molecular orbital plots were made using VMD[2] from the Gaussian output files.

S1: Synthesis and Sample Preparation

a. Synthesis scheme and details

Intermediate compounds **4**, **5**, **6**, **9**, and **10** were prepared following literature procedures.[3-8] Compound **7**, **8**, and **11**, although available in literature[9-10] were synthesized following different procedures. The ^{1}H NMR of all the intermediates agreed well with those available in literature.

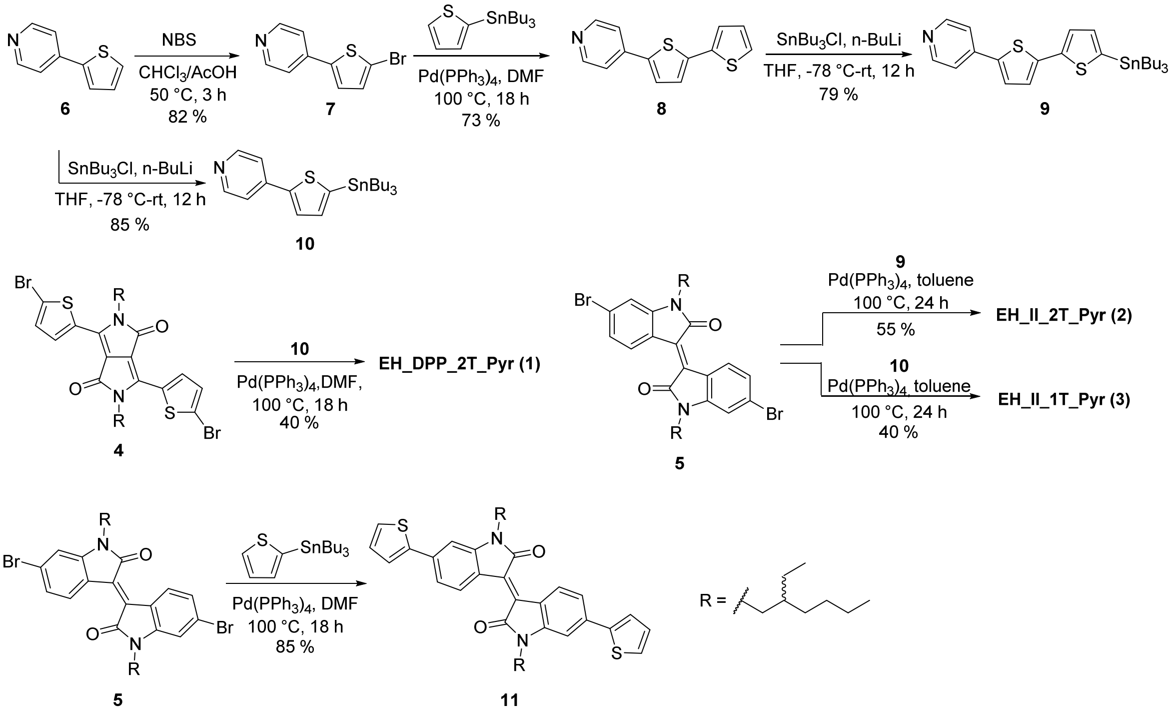
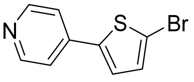
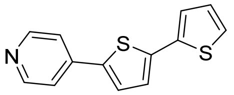


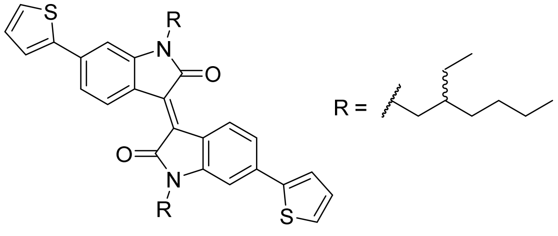
Fig. S1: Synthesis of the target compounds **1**, **2**, **3**, and test compound **11**.



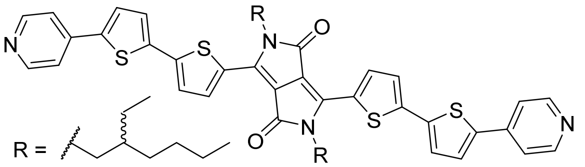
4-(5-Bromothiophen-2-yl)pyridine (7): To a 25 mL two-necked round-bottom flask was added **6** (0.35 g, 2.2 mmol) and NBS (0.43 g, 2.4 mmol) under argon atmosphere. A mixture of chloroform and acetic acid (1:1 = 15 mL) was injected with stirring and the mixture was heated to 50 °C and stirred for 3 h. After cooling to room temperature, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and the aqueous phase was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to give a light yellow solid (0.43 g, 1.8 mmol, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 (2H, d, J = 5.1 Hz), 7.46 (2H, d, J = 5.1 Hz), 7.31 (1H, d, J = 3.3 Hz), 7.13 (1H, d, J = 3.0 Hz) ppm. The ^{1}H NMR data match that found in the literature.[9]



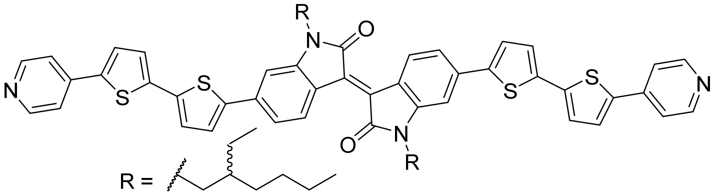
4-([2,2'-Bithiophen]-5-yl)pyridine (8): Under argon, 2-(tributylstannyl)thiophene (0.24 mL, 0.75 mmol) was added to a suspension of **7** (0.15 g, 0.63 mmol) and tetrakis(triphenylphosphine) palladium (0) (0.072g, 0.063 mmol) in DMF (10 mL). The solution was heated to 100 °C for 18 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The mixture was purified by flash column chromatography (ethyl acetate: hexanes = 1:1) followed by recrystallization from dichloromethane/hexanes to give a yellow solid (0.11 g, 0.46 mmol, 73 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.59 (2H, d, J = 6.0 Hz), 7.47 (2H, dd, J = 4.8 Hz, 1.5 Hz), 7.45 (1H, d, J = 3.6 Hz), 7.28 (2H, d, J = 5.1 Hz), 7.20 (1H, d, J = 3.9 Hz), 7.04 (1H, dd, J = 4.8 Hz, 3.6 Hz) ppm. The ^{1}H NMR data match that found in the literature.[9]



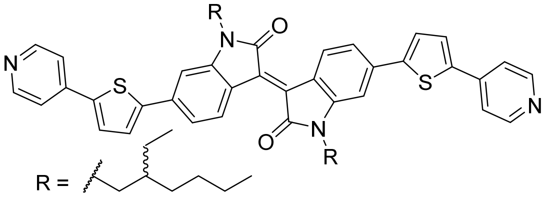
(*E*)-1,1'-Bis(2-ethylhexyl)-6,6'-di(thiophen-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (11): Under argon, 2-(tributylstannyl)thiophene (0.28 mL, 0.89 mmol) was added to a suspension of **5** (0.25 g, 0.39 mmol) and tetrakis(triphenylphosphine) palladium (0) (0.090g, 0.078 mmol) in DMF (10 mL). The solution was heated to 100 °C for 18 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The mixture was purified by flash column chromatography (dichloromethane: hexanes = 2:3) to give a brown solid **11** as a mixture of stereoisomers (*RR*, *SS*, *RS*) (0.22 g, 0.33 mmol, 85 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.15 (2H, d, J = 6.4 Hz), 7.42 (2H, d, J = 3.6 Hz), 7.36 (2H, d, J = 4.8 Hz), 7.30 (2H, d, J = 8.4 Hz), 7.13 (2H, t, J = 8.1 Hz), 6.96 (2H, s), 3.77 – 3.60 (4H, m), 1.94 – 1.78 (2H, m), 1.49 – 1.22 (16H, m), 1.00 – 0.87 (12H, m) ppm. The ^{1}H NMR data match that found in the literature.[10]



2,5-Bis(2-ethylhexyl)-3,6-bis(5'-(pyridin-4-yl)-[2,2'-bithiophen]-5-yl)-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4-dione (1): To a 25 mL three-necked round-bottom flask were added **4** (0.11 g, 0.16 mmol), **10** (0.15 g, 0.33 mmol), tetrakis(triphenylphosphine) palladium (0) (37 mg, 0.032 mmol), and anhydrous DMF (8 mL) under argon atmosphere. The mixture was stirred for 18 h at 100 °C. After cooling down to room temperature, the mixture was poured into cold acetone and filtered. The precipitate was further washed with acetone and was dried under vacuum to give a dark purple solid **1** as a mixture of stereoisomers (*RR*, *SS*, *RS*) (54 mg, 0.064 mmol, 40 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.94 (2H, d, J = 4.5 Hz), 8.63 (4H, d, J = 5.5 Hz), 7.48 (6H, d, J = 4.0 Hz), 7.37 (2H, d, J = 4.0 Hz), 7.33 (2H, d, J = 4.0 Hz), 4.10 – 4.01 (4H, m), 1.96 – 1.90 (2H, m), 1.42 – 1.25 (16H, m), 0.93 (6H, t, J = 7.5 Hz), 0.89 (6H, t, J = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): 161.5, 150.6, 141.9, 141.5, 140.5, 139.3, 137.8, 136.9, 128.9, 126.5, 126.2, 125.4, 119.6, 108.7, 46.1, 39.5, 30.5, 28.7, 23.9, 23.3, 14.3, 10.7 ppm. HRMS-ESI: *m/z* $[M+H]^+$calcd for $[C_{48}H_{51}N_4O_2S_4]^+$: 843.2889, found: 843.2847.



(*E*)-1,1'-Bis(2-ethylhexyl)-6,6'-bis(5'-(pyridin-4-yl)-[2,2'-bithiophen]-5-yl)-[3,3'-biindolinylidene]-2,2'-dione (2): Under argon, anhydrous toluene (10 mL) was added to a two-necked round-bottom flask containing **5** (0.10 g, 0.16 mmol), **9** (0.21 g, 0.39 mmol), and tetrakis(triphenylphosphine) palladium (0) (0.040 g, 0.032 mmol). The mixture was heated to 100 °C for 24 h. The reaction mixture was cooled to room temperature and poured into cold acetone. The precipitate obtained was filtered, washed with acetone, and dried under vacuum to give a dark brown solid. The solid was re-dissolved in chloroform, filtered to get rid of any insoluble particles, and evaporated to give a dark brown solid **2** as a mixture of stereoisomers (*RR*, *SS*, *RS*) (85 mg, 0.088 mmol, 55 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (2H, d, J = 8.5 Hz), 8.61 (4H, d, J = 5.5 Hz), 7.47 (4H, d, J = 5.5 Hz), 7.45 (2H, d, J = 4.0 Hz), 7.36 (2H, d, J = 3.5 Hz), 7.29 (2H, d, J = 8.5 Hz), 7.25 (4H, d, J = 4.0 Hz), 6.96 (2H, s), 3.80 – 3.68 (4H, m), 1.92 – 1.90 (2H, m), 1.49 – 1.34 (16H, m), 1.00 (6H, t, J = 7.5 Hz), 0.94 (6H, t, J = 7.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 150.7, 146.0, 143.9, 141.0, 140.2, 139.0, 137.4, 137.2, 132.0, 130.6, 126.3, 125.5, 125.3, 125.2, 121.5, 119.5, 119.1, 105.8, 44.4, 38.1, 31.1, 29.1, 24.6, 23.3, 14.3, 11.0 ppm. HRMS-ESI: *m/z* $[M+H]^+$calcd for $(C_{58}H_{56}N_4O_2S_4)^+$ calcd: 969.3359, found: 969.3320.



(*E*)-1,1'-Bis(2-ethylhexyl)-6,6'-bis(5-(pyridin-4-yl)thiophen-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (3): Under argon, anhydrous toluene (10 mL) was added to a two-necked round-bottom flask containing **5** (0.10 g, 0.16 mmol), **10** (0.21 g, 0.47 mmol), and tetrakis(triphenylphosphine) palladium (0) (0.036 g, 0.032 mmol). The mixture was heated to 100 °C for 24 h. The reaction mixture was cooled to room temperature and poured into cold acetone. The precipitate obtained was filtered, washed with acetone, and dried under vacuum to give a dark brown solid. The solid was re-dissolved in chloroform, filtered to get rid of any insoluble particles, and evaporated to give a dark brown solid **3** as a mixture of stereoisomers (*RR*, *SS*, *RS*) (52 mg, 0.064 mmol, 40 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (2H, d, *J* = 9.0 Hz), 8.62 (4H, d, *J* = 6.0 Hz), 7.52 (2H, d, *J* = 4.0 Hz), 7.50 (4H, d, *J* = 6.0 Hz), 7.43 (2H, d, *J* = 4.0 Hz), 7.33 (2H, d, *J* = 9.0 Hz), 6.99 (2H, s), 3.79 – 3.67 (4H, m), 1.93 – 1.87 (2H, m), 1.48-1.32 (16, m), 0.98 (6H, t, *J* = 6.5 Hz), 0.93 (6H, t, *J* = 7.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 150.7, 146.0, 145.8, 141.5, 141.0, 137.2, 132.3, 130.6, 126.7, 125.6, 121.8, 119.7, 119.5, 105.1, 44.3, 38.0, 31.0, 29.0, 24.4, 23.3, 14.3, 11.0 ppm. HRMS-ESI: *m/z* $[M+H]^+$calcd for $(C_{50}H_{52}N_4O_2S_2)^+$ calcd: 805.3604, found: 805.3607.

b. Sample preparation for titration study with metals:

Each compound was dissolved in THF (10 μM) and the metal was dissolved in DMF (0.98 mM). The sample for analysis was prepared by mixing 9.8 mL THF (containing compound) + 0.2 mL of DMF (containing 2 equiv of metal). **Metals used**: $AlCl_3$, LiCl, $CaCl_2$, $ZnCl_2$, $Co(OAc)_2 \cdot 4H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, $Pd(dba)_2$, $Pd(OAc)_2$, $CuCl_2$.

S2: Disorder observed in the alkyl chain of crystal structure of compound 2

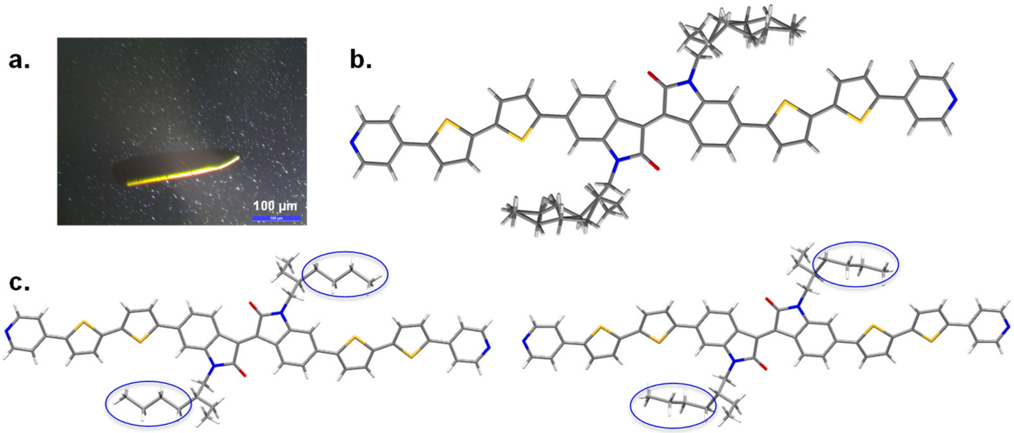


Fig. S2: **a**. Optical microscopy image of the crystal of compound **2.** **b**. X-ray crystal structure showing the disorder observed in the alkyl side chains. **c**. Fully refined two parts showing the disorder in the alkyl groups, **left image**: circled alkyl chain is in the plane of the π-system; **right image**: circled alkyl chain is perpendicular to the plane of the π-system.

S3: HOMO and LUMO frontier molecular orbital plots of compound 3

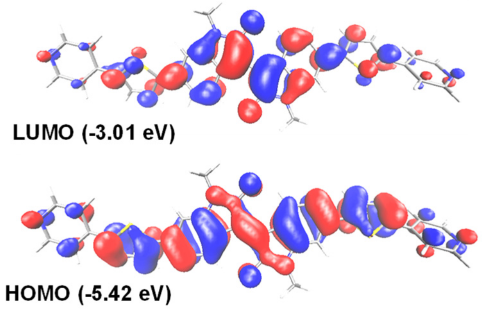


Fig. S3: HOMO (bottom) and LUMO (top) frontier molecular orbitals of **3** based on gas phase DFT calculations (B3LYP/6-31G*). 2-Ethylhexyl groups have been truncated to methyl groups for the calculation.

S4: Conformational analysis

a. Gas phase energy and dihedral angle comparisons

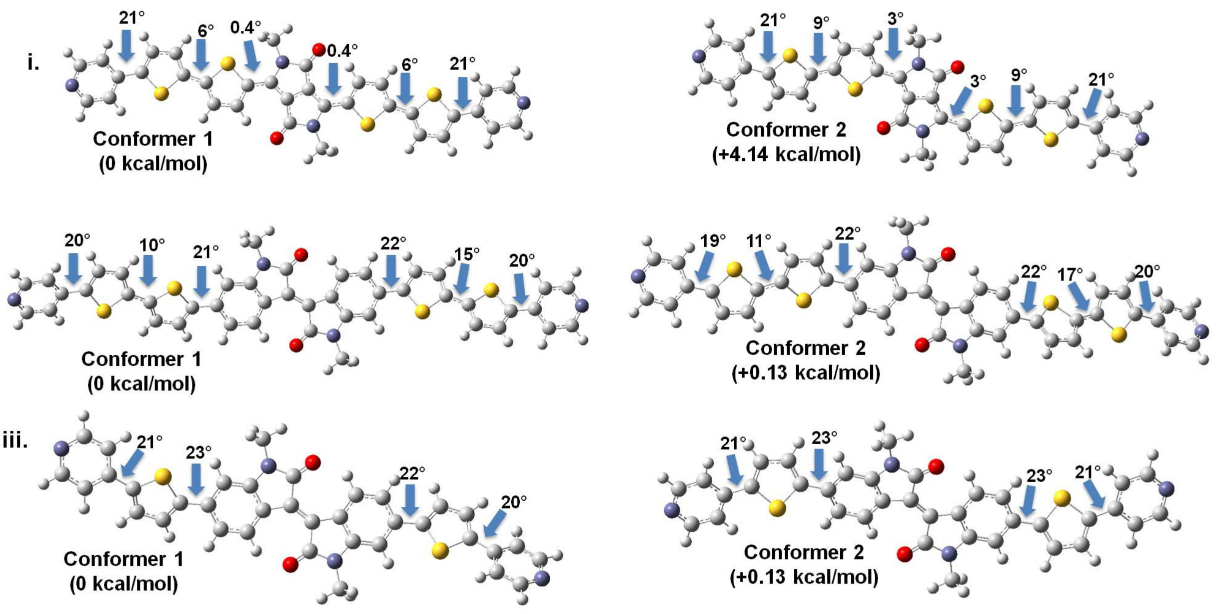


Fig. S4a: Energy and dihedral angle comparisons between the different conformations of (i) compound **1**, (ii) compound **2**, and (iii) compound **3** at the B3LYP/6-31G* level of theory.

b. Molecular planarity comparison of compound 2 in solid state and gas phase

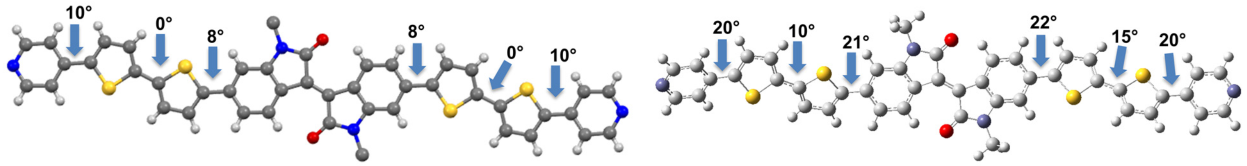


Fig. S4b: Comparison of the torsions of compound **2** obtained from X-ray (left) and DFT calculation (right)

S5: UV-Vis absorption spectra in THF

Absorption spectra were measured for five different concentrations (2.5 – 20 μM) of the compounds on a Cary 100 Bio UV-Visible spectrophotometer using 1 cm quartz cells. The absorption intensity at λ_{max} was then plotted against the concentration in all cases to confirm, by linearity, whether the compounds followed Beer's law. Molar extinction coefficients (ε) were determined from the linear plot for each compound (where $A = \varepsilon bc$).

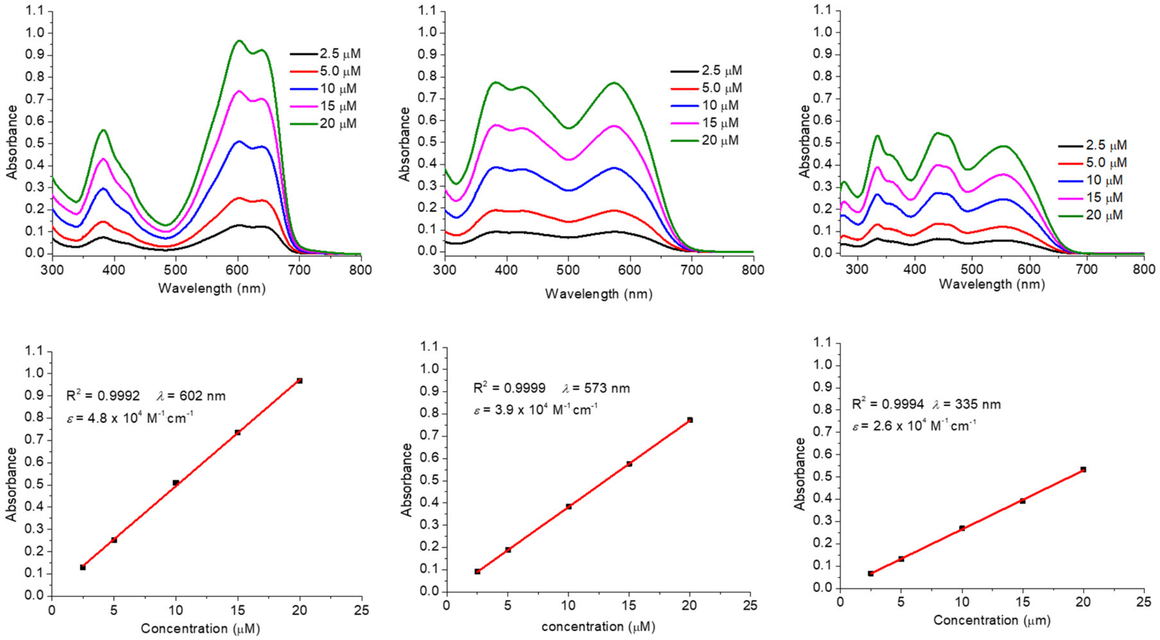


Fig. S5: Absorption spectra (top) and Beer-Lambert plots (bottom) of **1** (left), **2** (middle), and **3** (right) in THF

S6: Fluorescence spectra of 11 and 8

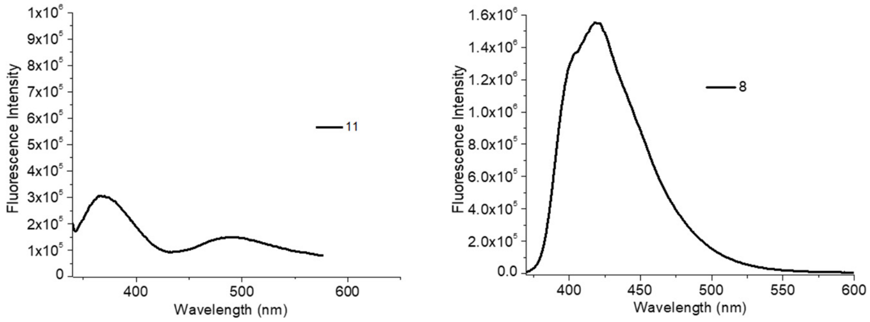
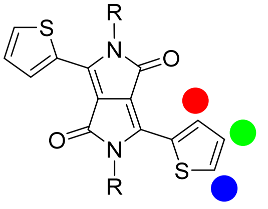


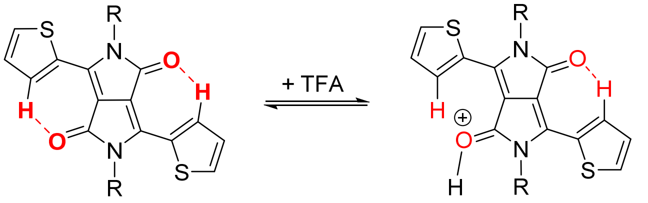
Fig. S6: Fluorescence spectra of compound **11** (left) and **8** (right) in THF (10 μM). $\lambda_{excitation}$ of **11** = 310 nm and **8** = 350 nm.

S7: Protonation of core units (4/5) and end group (8) with TFA: Analysis by ^1H NMR ($CDCl_3$)

a. Diketopyrrolopyrrole core unit (**4**)



Compound 4



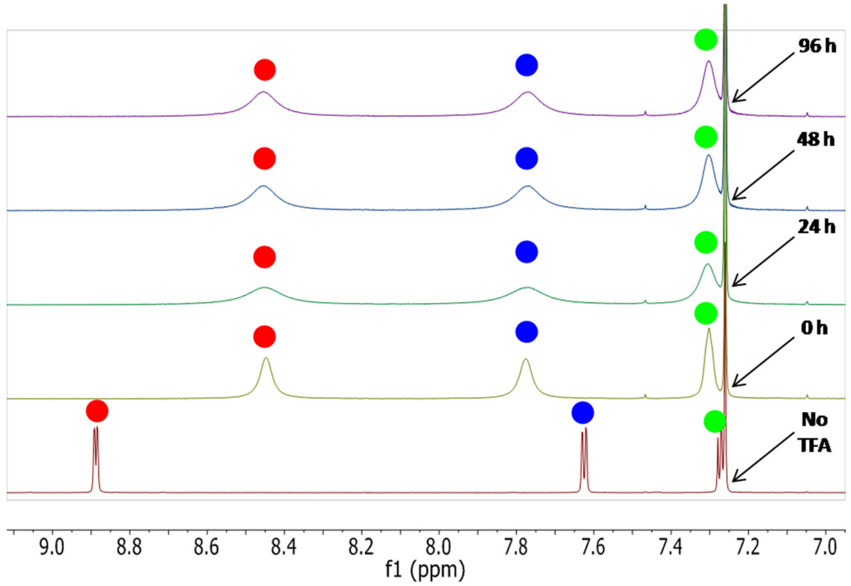
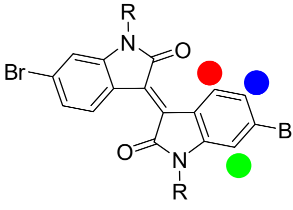
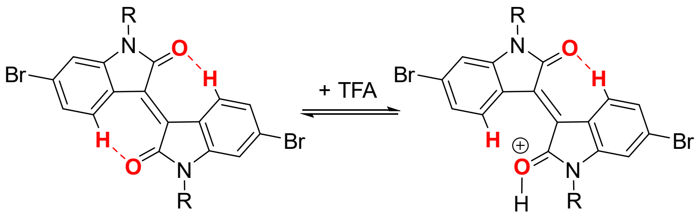


Fig. S7a: ^{1}H NMR spectra (aromatic region) of compound **4** in the presence of 9000 equiv of TFA in CDCl$_3$.

b. Isoindigo core unit (**5**)



Compound 5



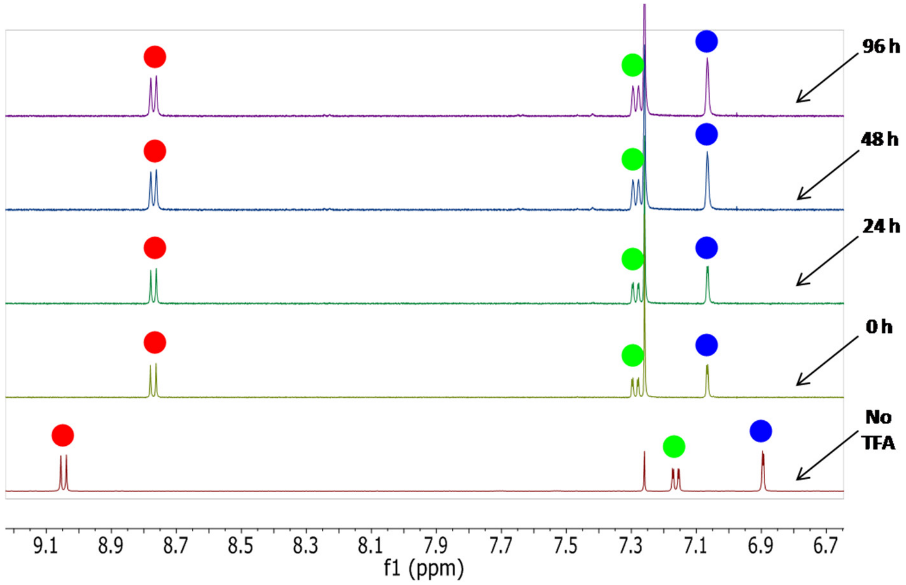


Fig. S7b: ^{1}H NMR spectra (aromatic region) of compound **5** in the presence of 9000 equiv of TFA in CDCl$_3$.

c. Pyridine bithiophene end group (**8**)

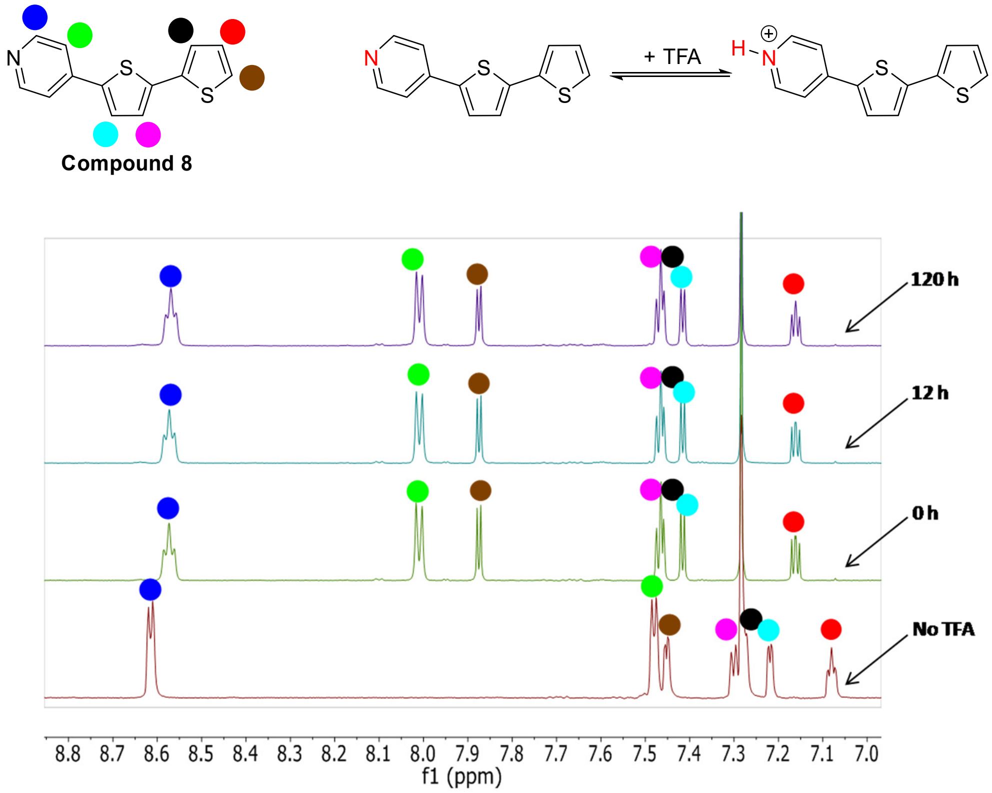


Fig. S7c: ^{1}H NMR spectra (aromatic region) of compound **8** in the presence of 9000 equiv of TFA in $CDCl_3$.

S8: Predicted multi-protonation states of compounds 1 and 2

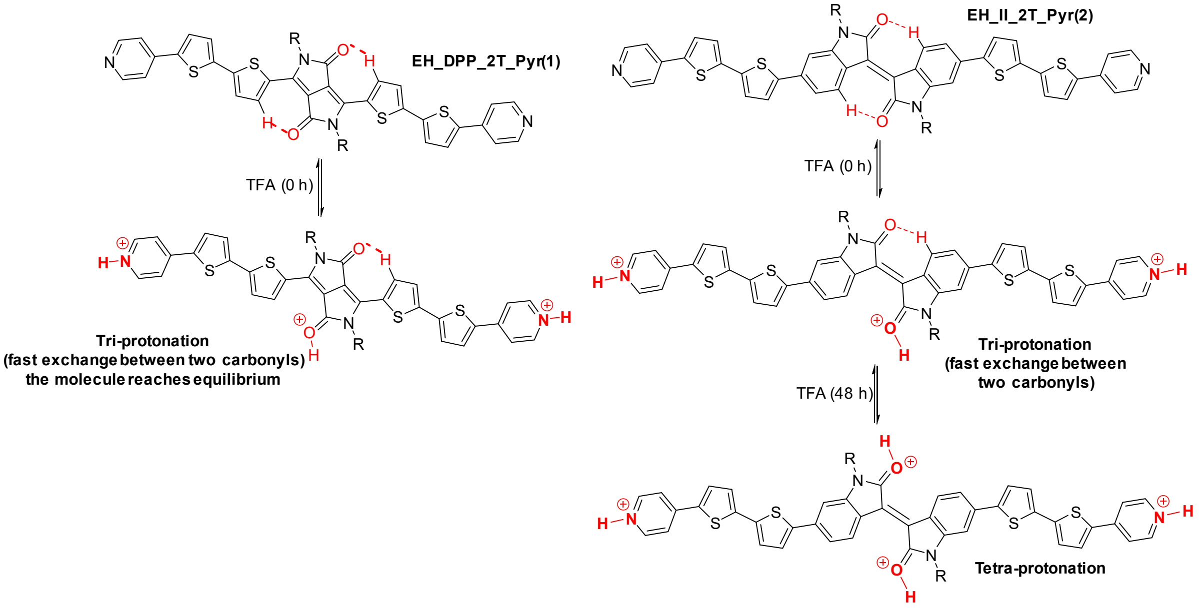


Fig. S8: Scheme which shows the predicted multi-protonation states of **1** (left) and **2** (right).

S9a: Titration of compound 3 with TFA in THF

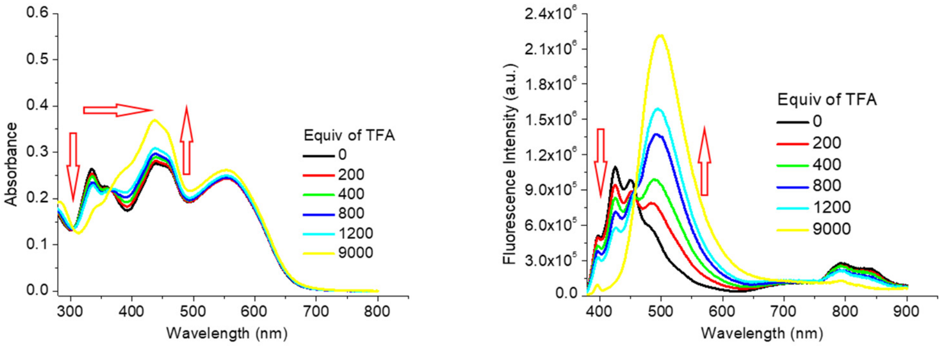
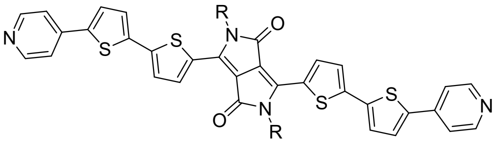


Figure S9a: Absorption (left) and fluorescence (right) spectra generated upon titration of compound **3** with TFA in THF. $\lambda_{\text{excitation}} = 355$ nm.

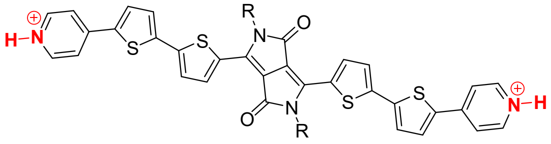
S9b: Gas phase DFT calculation of target compounds upon protonation of pyridine units

Before Protonation

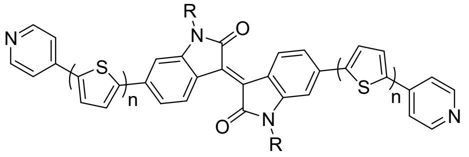


EH_DPP_2T_Pyr (1)

After Protonation

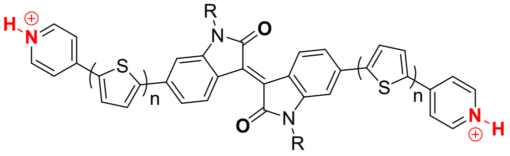


Protonated 1



n = 2: EH_II_2T_Pyr (2)

n = 1: EH_II_1T_Pyr (3)



n = 2: Protonated 2

n = 1: Protonated 3

	Before protonation			**After protonation**		
Compound	LUMO (eV)	HOMO (eV)	E_{HL} (eV)	LUMO (eV)	HOMO (eV)	E_{HL} (eV)
1	-2.96	-4.95	1.99	-7.22	-8.57	1.35
2	-2.98	-5.21	2.23	-6.66	-8.36	1.70
3	-3.01	-5.42	2.41	-7.20	-9.17	1.97

Table S9b: Table showing the calculated HOMO/LUMO values of compound **1**, **2**, and **3** before and after protonation of pyridine units (performed at the level of B3LYP/6-31G* with frequency optimizations).

S10: Titration of compound 3 with Pd^{2+} in THF

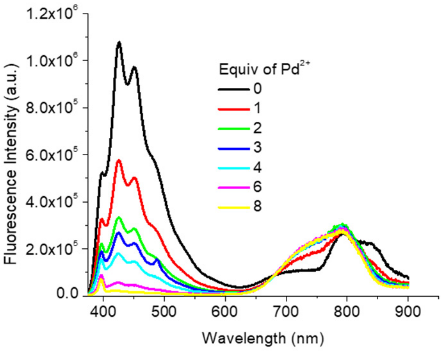


Fig. S10: Fluorescence spectra of **3** in THF as a function of different equiv of Pd^{2+}. $\lambda_{excitation}$ = 355 nm.

S11: Stern-Volmer plots of compounds 1, 2, and 3

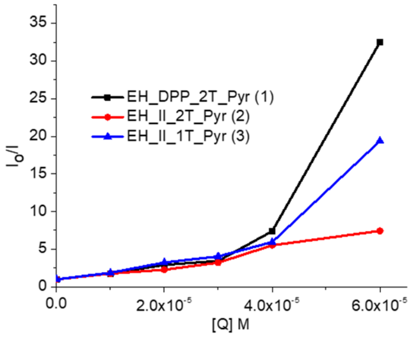


Fig. S11: Stern-Volmer plots of **1**, **2**, and **3** upon titration with Pd^{2+} ion in THF. The fluorescence intensity was monitored at λ = 673 nm for **1**, λ = 500 nm for **2**, and λ = 425 nm for **3**.

S12: Fluorescence spectra (THF) of core units (4/11) and end group (8)

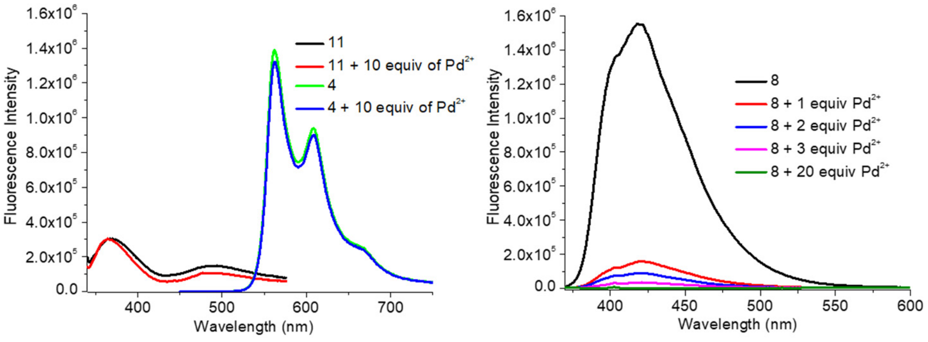


Fig. S12: Fluorescence spectra of compound **4/11** (left) and **8** (right) in THF as a function of different equiv of Pd^{2+}. $\lambda_{excitation}$ of compound **4** = 340 nm, compound **11** = 310 nm, and compound **8** = 350 nm.

Note: A very wide slit was used for compound **11** (slit width = 2mm) due to the low fluorescence intensity of the compound. This resulted in a slight variation between the two bands.

S13: X-ray experimental of compound 2

X-ray intensity data were collected at 100 K on a Bruker **DUO** diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consisted of one half of the molecule, where the other half of the molecule is related by inversion. The 2-ethylhexyl group was partially disordered and refined in two parts, where the site occupation factors were dependently refined to 0.505(2) and 0.495(2), respectively. In the final cycle of refinement, 5479 reflections (of which 4053 are observed with I > 2σ(I)) were used to refine 323 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 4.56%, 11.54% and 1.008, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized. *SHELXTL2014* (2014). Bruker-AXS, Madison, Wisconsin, USA.

Table S13. Crystal data and structure refinement for compound **2**.

Identification code	asme7	
CCDC number	1865380	
Empirical formula	C29 H28 N2 O S2	
Formula weight	484.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 17.6070(12) Å	α= 90°.
	b = 5.4871(4) Å	β= 106.1690(15)°.
	c = 25.7682(17) Å	γ = 90°.
Volume	2391.0(3) Å^3	
Z	4	
Density (calculated)	1.346 Mg/m^3	

Absorption coefficient	0.249 mm^{-1}
F(000)	1024
Crystal size	0.236 x 0.069 x 0.021 mm^3
Theta range for data collection	1.255 to 27.499°.
Index ranges	$-22 \leq h \leq 22$, $-6 \leq k \leq 7$, $-33 \leq l \leq 33$
Reflections collected	35017
Independent reflections	5479 [R(int) = 0.0446]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Analytical
Max. and min. transmission	0.9951 and 0.9679
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5479 / 1 / 323
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1154 [4053]
R indices (all data)	R1 = 0.0677, wR2 = 0.1232
Extinction coefficient	n/a
Largest diff. peak and hole	0.916 and -0.331 e.$Å^{-3}$

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	6288(1)	6146(1)	5782(1)	26(1)
S2	4035(1)	3460(1)	5970(1)	22(1)
O1	10480(1)	9032(3)	5603(1)	31(1)
N1	9254(1)	8081(3)	5674(1)	22(1)
N2	1529(1)	4230(4)	6796(1)	35(1)
C1	9898(1)	7723(4)	5482(1)	23(1)
C2	9728(1)	5498(4)	5114(1)	22(1)
C3	8909(1)	4831(4)	5092(1)	21(1)

C4	8360(1)	3079(4)	4819(1)	26(1)
C5	7627(1)	2897(4)	4915(1)	26(1)
C6	7402(1)	4422(4)	5280(1)	21(1)
C7	7929(1)	6251(4)	5544(1)	21(1)
C8	8658(1)	6403(4)	5445(1)	21(1)
C9	6639(1)	4073(4)	5398(1)	21(1)
C10	6123(1)	2158(4)	5252(1)	24(1)
C11	5453(1)	2368(4)	5448(1)	24(1)
C12	5449(1)	4430(4)	5744(1)	21(1)
C13	4867(1)	5210(4)	6012(1)	22(1)
C14	4857(1)	7259(4)	6314(1)	29(1)
C15	4191(1)	7402(4)	6512(1)	29(1)
C16	3684(1)	5475(4)	6364(1)	21(1)
C17	2946(1)	5020(4)	6507(1)	23(1)
C18	2425(1)	3149(4)	6281(1)	32(1)
C19	1738(1)	2837(5)	6436(1)	36(1)
C20	2738(1)	6468(4)	6889(1)	34(1)
C21	2040(2)	6015(4)	7016(1)	40(1)
C22	9176(1)	10100(4)	6024(1)	25(1)
C23	9273(1)	9390(5)	6617(1)	37(1)
C24	10101(2)	8722(5)	6911(1)	40(1)
C25	10196(2)	7419(5)	7449(1)	47(1)
C26	9021(8)	11712(12)	6858(6)	42(2)
C27	8100(3)	12309(9)	6745(2)	35(1)
C28	7651(3)	10654(11)	7017(2)	40(1)
C29	6750(30)	11260(110)	6900(20)	58(3)
C26'	8844(7)	11091(13)	6914(5)	42(2)
C27'	7981(3)	10523(9)	6744(2)	35(1)
C28'	7548(3)	12167(11)	7031(2)	40(1)
C29'	6680(30)	11470(110)	6870(20)	58(3)

Table 3. Bond lengths [Å] and angles [°] for compound **2**.

S1-C9	1.730(2)
S1-C12	1.730(2)

S2-C16	1.728(2)
S2-C13	1.729(2)
O1-C1	1.220(2)
N1-C1	1.371(3)
N1-C8	1.397(2)
N1-C22	1.458(3)
N2-C19	1.331(3)
N2-C21	1.344(3)
C1-C2	1.525(3)
C2-C2#1	1.369(4)
C2-C3	1.474(3)
C3-C4	1.405(3)
C3-C8	1.410(3)
C4-C5	1.384(3)
C4-H4A	0.9500
C5-C6	1.397(3)
C5-H5A	0.9500
C6-C7	1.406(3)
C6-C9	1.470(3)
C7-C8	1.381(3)
C7-H7A	0.9500
C9-C10	1.371(3)
C10-C11	1.411(3)
C10-H10A	0.9500
C11-C12	1.366(3)
C11-H11A	0.9500
C12-C13	1.451(3)
C13-C14	1.371(3)
C14-C15	1.405(3)
C14-H14A	0.9500
C15-C16	1.368(3)
C15-H15A	0.9500
C16-C17	1.468(3)
C17-C18	1.391(3)
C17-C20	1.390(3)
C18-C19	1.385(3)

C18-H18A	0.9500
C19-H19A	0.9500
C20-C21	1.380(3)
C20-H20A	0.9500
C21-H21A	0.9500
C22-C23	1.538(3)
C22-H22A	0.9900
C22-H22B	0.9900
C23-C24	1.488(3)
C23-C26'	1.533(4)
C23-C26	1.538(5)
C23-H23A	1.0000
C23-H23B	1.0000
C24-C25	1.526(3)
C24-H24A	0.9900
C24-H24B	0.9900
C25-H25A	0.9800
C25-H25B	0.9800
C25-H25C	0.9800
C26-C27	1.599(13)
C26-H26A	0.9900
C26-H26B	0.9900
C27-C28	1.500(8)
C27-H27A	0.9900
C27-H27B	0.9900
C28-C29	1.56(5)
C28-H28A	0.9900
C28-H28B	0.9900
C29-H29A	0.9800
C29-H29B	0.9800
C29-H29C	0.9800
C26'-C27'	1.493(12)
C26'-H26C	0.9900
C26'-H26D	0.9900
C27'-C28'	1.501(7)
C27'-H27C	0.9900

C27'-H27D	0.9900
C28'-C29'	1.51(5)
C28'-H28C	0.9900
C28'-H28D	0.9900
C29'-H29D	0.9800
C29'-H29E	0.9800
C29'-H29F	0.9800

C9-S1-C12	92.61(9)
C16-S2-C13	92.48(10)
C1-N1-C8	110.56(16)
C1-N1-C22	124.11(16)
C8-N1-C22	125.03(17)
C19-N2-C21	115.4(2)
O1-C1-N1	123.01(19)
O1-C1-C2	129.46(19)
N1-C1-C2	107.53(16)
C2#1-C2-C3	132.8(2)
C2#1-C2-C1	123.1(2)
C3-C2-C1	104.03(16)
C4-C3-C8	116.57(18)
C4-C3-C2	135.85(19)
C8-C3-C2	107.59(17)
C5-C4-C3	120.31(19)
C5-C4-H4A	119.8
C3-C4-H4A	119.8
C4-C5-C6	122.09(19)
C4-C5-H5A	119.0
C6-C5-H5A	119.0
C5-C6-C7	118.73(18)
C5-C6-C9	120.54(18)
C7-C6-C9	120.71(18)
C8-C7-C6	118.43(19)
C8-C7-H7A	120.8
C6-C7-H7A	120.8
C7-C8-N1	126.09(18)

C7-C8-C3	123.81(18)
N1-C8-C3	110.10(17)
C10-C9-C6	128.10(19)
C10-C9-S1	110.21(15)
C6-C9-S1	121.67(15)
C9-C10-C11	113.30(18)
C9-C10-H10A	123.3
C11-C10-H10A	123.3
C12-C11-C10	113.66(18)
C12-C11-H11A	123.2
C10-C11-H11A	123.2
C11-C12-C13	128.61(18)
C11-C12-S1	110.22(15)
C13-C12-S1	121.17(15)
C14-C13-C12	129.43(18)
C14-C13-S2	110.25(15)
C12-C13-S2	120.32(15)
C13-C14-C15	113.38(19)
C13-C14-H14A	123.3
C15-C14-H14A	123.3
C16-C15-C14	113.61(19)
C16-C15-H15A	123.2
C14-C15-H15A	123.2
C15-C16-C17	128.01(19)
C15-C16-S2	110.27(15)
C17-C16-S2	121.72(15)
C18-C17-C20	116.4(2)
C18-C17-C16	123.14(19)
C20-C17-C16	120.43(19)
C19-C18-C17	119.8(2)
C19-C18-H18A	120.1
C17-C18-H18A	120.1
N2-C19-C18	124.2(2)
N2-C19-H19A	117.9
C18-C19-H19A	117.9
C21-C20-C17	119.5(2)

C21-C20-H20A	120.3
C17-C20-H20A	120.3
N2-C21-C20	124.6(2)
N2-C21-H21A	117.7
C20-C21-H21A	117.7
N1-C22-C23	114.65(18)
N1-C22-H22A	108.6
C23-C22-H22A	108.6
N1-C22-H22B	108.6
C23-C22-H22B	108.6
H22A-C22-H22B	107.6
C24-C23-C26'	116.3(6)
C24-C23-C26	110.4(6)
C24-C23-C22	113.0(2)
C26'-C23-C22	114.0(6)
C26-C23-C22	103.1(5)
C24-C23-H23A	110.0
C26-C23-H23A	110.0
C22-C23-H23A	110.0
C24-C23-H23B	103.9
C26'-C23-H23B	103.9
C22-C23-H23B	103.9
C23-C24-C25	115.0(2)
C23-C24-H24A	108.5
C25-C24-H24A	108.5
C23-C24-H24B	108.5
C25-C24-H24B	108.5
H24A-C24-H24B	107.5
C24-C25-H25A	109.5
C24-C25-H25B	109.5
H25A-C25-H25B	109.5
C24-C25-H25C	109.5
H25A-C25-H25C	109.5
H25B-C25-H25C	109.5
C23-C26-C27	119.2(8)
C23-C26-H26A	107.5

C27-C26-H26A	107.5
C23-C26-H26B	107.5
C27-C26-H26B	107.5
H26A-C26-H26B	107.0
C28-C27-C26	115.5(5)
C28-C27-H27A	108.4
C26-C27-H27A	108.4
C28-C27-H27B	108.4
C26-C27-H27B	108.4
H27A-C27-H27B	107.5
C27-C28-C29	115(2)
C27-C28-H28A	108.6
C29-C28-H28A	108.6
C27-C28-H28B	108.6
C29-C28-H28B	108.6
H28A-C28-H28B	107.5
C28-C29-H29A	109.5
C28-C29-H29B	109.5
H29A-C29-H29B	109.5
C28-C29-H29C	109.5
H29A-C29-H29C	109.5
H29B-C29-H29C	109.5
C27'-C26'-C23	109.3(6)
C27'-C26'-H26C	109.8
C23-C26'-H26C	109.8
C27'-C26'-H26D	109.8
C23-C26'-H26D	109.8
H26C-C26'-H26D	108.3
C26'-C27'-C28'	110.2(4)
C26'-C27'-H27C	109.6
C28'-C27'-H27C	109.6
C26'-C27'-H27D	109.6
C28'-C27'-H27D	109.6
H27C-C27'-H27D	108.1
C27'-C28'-C29'	109(2)
C27'-C28'-H28C	109.9

C29'-C28'-H28C	109.9
C27'-C28'-H28D	109.9
C29'-C28'-H28D	109.9
H28C-C28'-H28D	108.3
C28'-C29'-H29D	109.5
C28'-C29'-H29E	109.5
H29D-C29'-H29E	109.5
C28'-C29'-H29F	109.5
H29D-C29'-H29F	109.5
H29E-C29'-H29F	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for compound **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

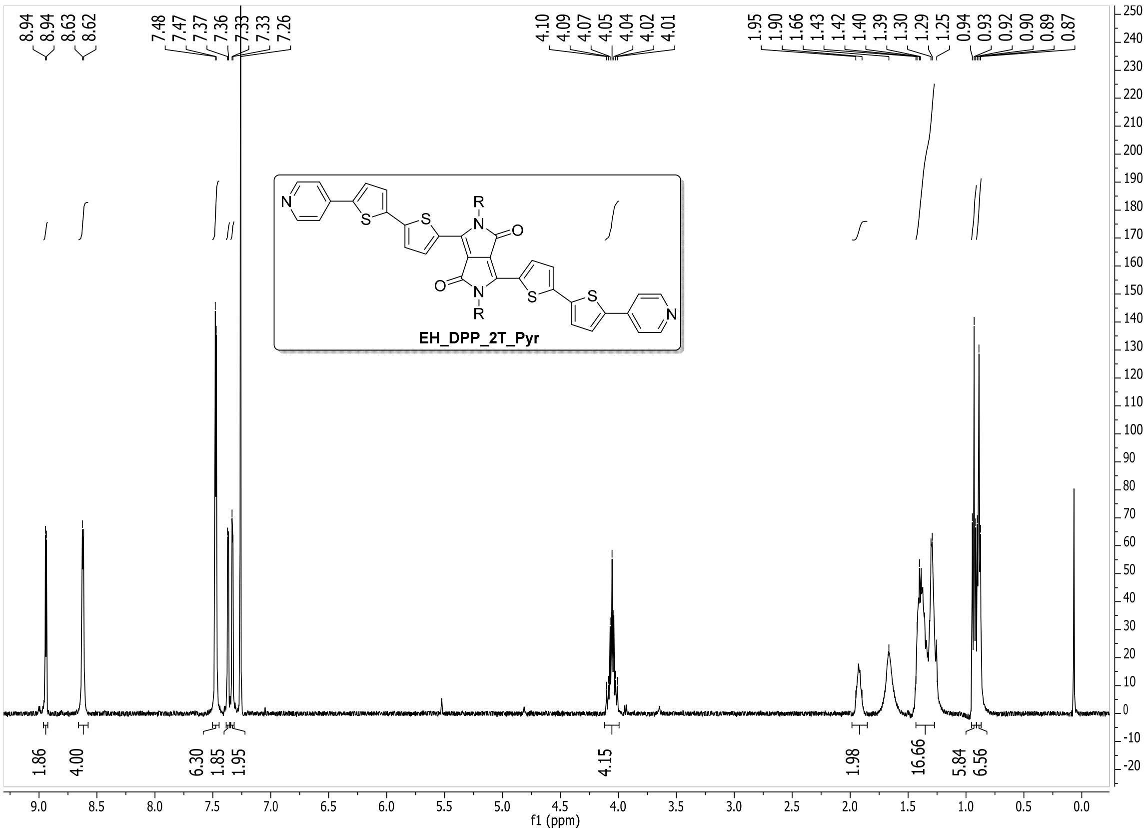
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	23(1)	20(1)	37(1)	-5(1)	10(1)	-7(1)
S2	20(1)	21(1)	27(1)	-4(1)	6(1)	-4(1)
O1	25(1)	33(1)	36(1)	-11(1)	11(1)	-15(1)
N1	20(1)	21(1)	23(1)	-2(1)	3(1)	-6(1)
N2	31(1)	34(1)	45(1)	-2(1)	18(1)	-2(1)
C1	23(1)	25(1)	19(1)	1(1)	5(1)	-6(1)
C2	23(1)	26(1)	15(1)	1(1)	2(1)	-10(1)
C3	19(1)	28(1)	16(1)	1(1)	4(1)	-8(1)
C4	24(1)	34(1)	21(1)	-7(1)	6(1)	-9(1)
C5	21(1)	33(1)	21(1)	-7(1)	3(1)	-13(1)
C6	17(1)	24(1)	18(1)	2(1)	2(1)	-5(1)
C7	20(1)	22(1)	20(1)	1(1)	4(1)	-5(1)
C8	20(1)	21(1)	17(1)	3(1)	0(1)	-6(1)
C9	18(1)	23(1)	18(1)	0(1)	2(1)	-3(1)
C10	23(1)	26(1)	24(1)	-7(1)	7(1)	-6(1)
C11	20(1)	25(1)	27(1)	-5(1)	5(1)	-9(1)
C12	16(1)	21(1)	24(1)	1(1)	2(1)	-4(1)

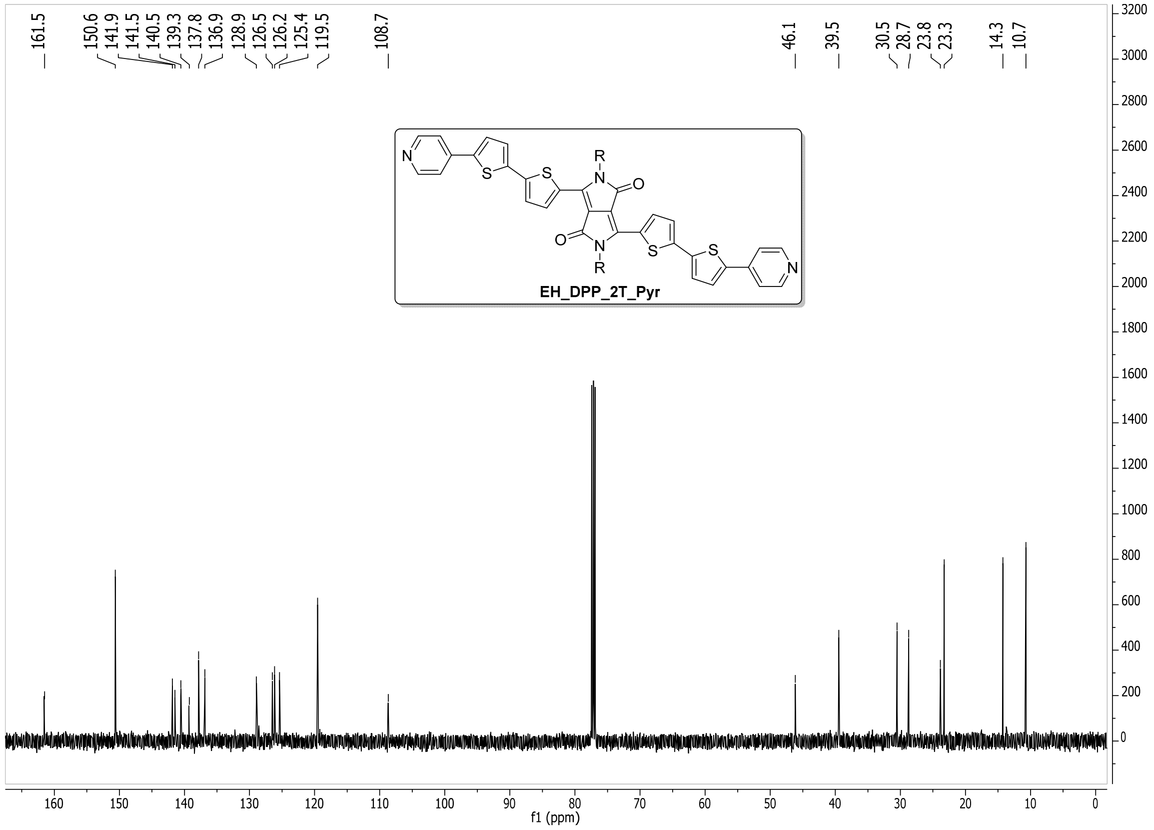
C13	17(1)	21(1)	25(1)	1(1)	3(1)	-3(1)
C14	28(1)	22(1)	38(1)	-7(1)	12(1)	-8(1)
C15	32(1)	22(1)	34(1)	-6(1)	12(1)	-3(1)
C16	23(1)	19(1)	21(1)	1(1)	5(1)	1(1)
C17	24(1)	22(1)	22(1)	2(1)	7(1)	1(1)
C18	31(1)	34(1)	35(1)	-12(1)	14(1)	-7(1)
C19	30(1)	38(1)	41(1)	-9(1)	13(1)	-12(1)
C20	37(1)	27(1)	44(1)	-9(1)	18(1)	-8(1)
C21	42(1)	34(1)	52(2)	-11(1)	27(1)	-5(1)
C22	22(1)	23(1)	30(1)	-4(1)	4(1)	-4(1)
C23	40(1)	43(1)	24(1)	-8(1)	2(1)	-1(1)
C24	39(1)	43(1)	39(1)	1(1)	11(1)	1(1)
C25	55(2)	54(2)	29(1)	4(1)	8(1)	1(1)
C26	29(5)	74(4)	26(3)	-3(3)	13(2)	9(3)
C27	43(2)	33(2)	30(2)	-4(2)	9(1)	1(2)
C28	41(2)	42(2)	34(2)	-3(2)	6(2)	8(2)
C29	47(7)	80(8)	40(4)	5(4)	0(5)	-6(5)
C26'	29(5)	74(4)	26(3)	-3(3)	13(2)	9(3)
C27'	43(2)	33(2)	30(2)	-4(2)	9(1)	1(2)
C28'	41(2)	42(2)	34(2)	-3(2)	6(2)	8(2)
C29'	47(7)	80(8)	40(4)	5(4)	0(5)	-6(5)

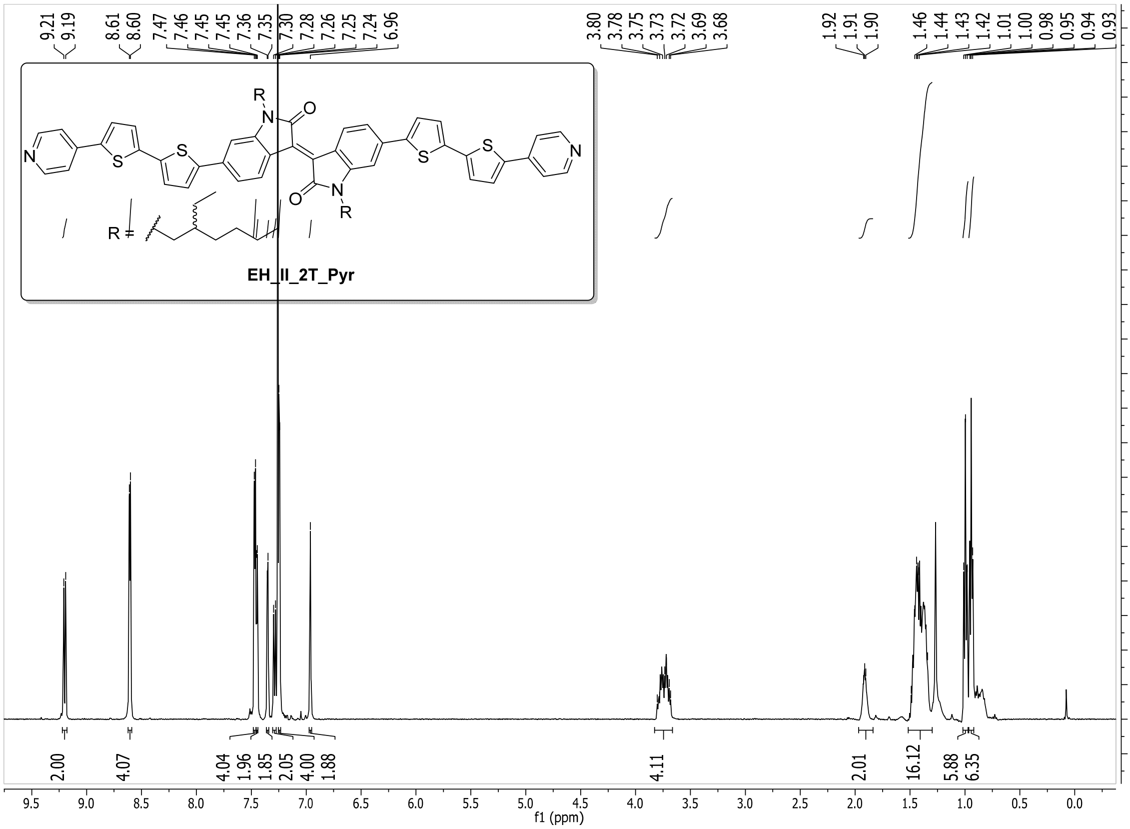
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **2**.

	x	y	z	U(eq)
H4A	8493	2015	4567	32
H5A	7266	1697	4727	31
H7A	7785	7355	5785	25
H10A	6208	823	5040	29
H11A	5043	1185	5380	29
H14A	5260	8464	6382	35
H15A	4102	8713	6729	34

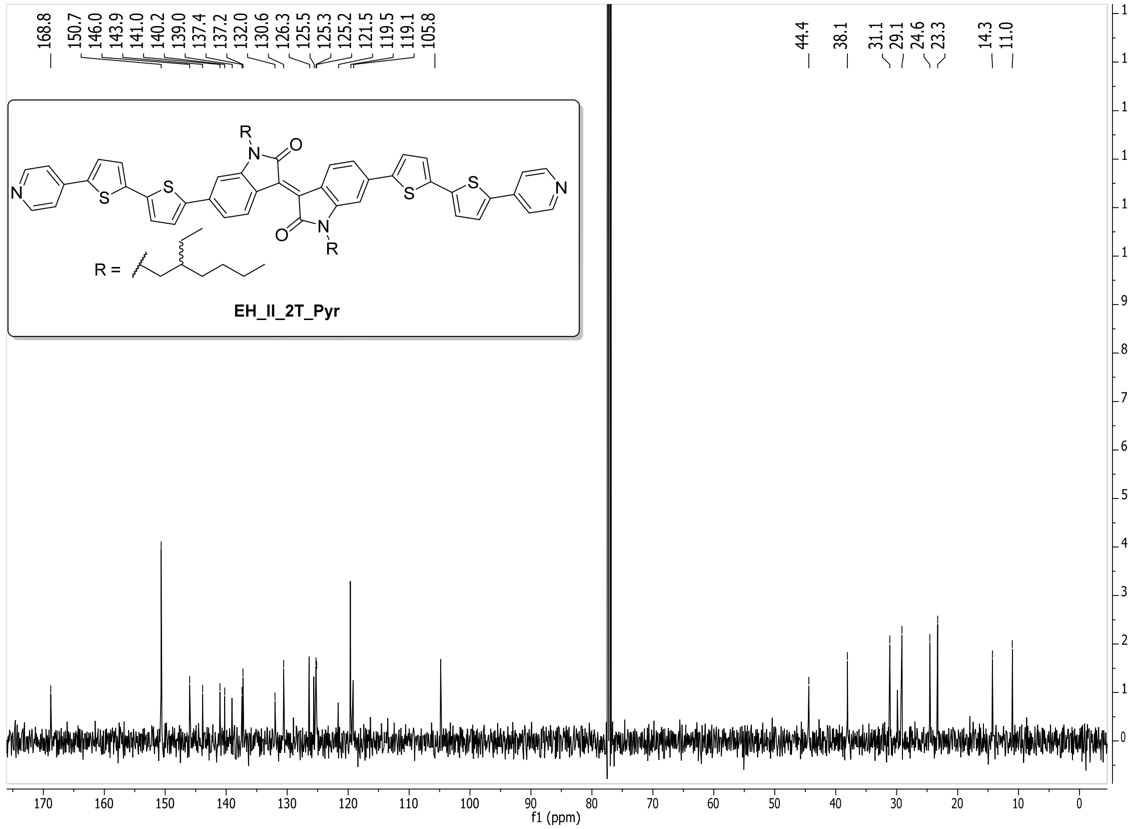
H18A	2541	2088	6022	39
H19A	1394	1544	6274	43
H20A	3074	7758	7061	41
H21A	1911	7037	7277	48
H22A	8649	10852	5877	30
H22B	9578	11349	6014	30
H23A	8908	8018	6635	45
H23B	8978	7818	6590	45
H24A	10424	10227	6979	49
H24B	10315	7660	6675	49
H25A	10756	7041	7613	70
H25B	9889	5905	7387	70
H25C	10005	8476	7692	70
H26A	9270	13115	6727	50
H26B	9251	11635	7255	50
H27A	8046	14002	6862	42
H27B	7851	12234	6350	42
H28A	7897	10734	7412	48
H28B	7706	8959	6901	48
H29A	6690	12952	6999	87
H29B	6515	10171	7113	87
H29C	6492	11021	6515	87
H26C	9058	10868	7309	50
H26D	8930	12809	6827	50
H27C	7898	8802	6831	42
H27D	7769	10744	6349	42
H28C	7606	13884	6931	48
H28D	7773	12005	7427	48
H29D	6621	9881	7031	87
H29E	6486	11362	6478	87
H29F	6380	12700	7005	87


8.94
8.94
8.63
8.62
7.48
7.47
7.37
7.36
7.33
7.33
7.26
4.10
4.09
4.07
4.05
4.04
4.02
4.01
1.95
1.90
1.66
1.43
1.42
1.40
1.39
1.30
1.29
1.25
0.94
0.93
0.92
0.90
0.89
0.87
EH_DPP_2T_Pyr
N
S
R
O
1.86
4.00
6.30
1.85
1.95
4.15
1.98
16.66
5.84
6.56
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

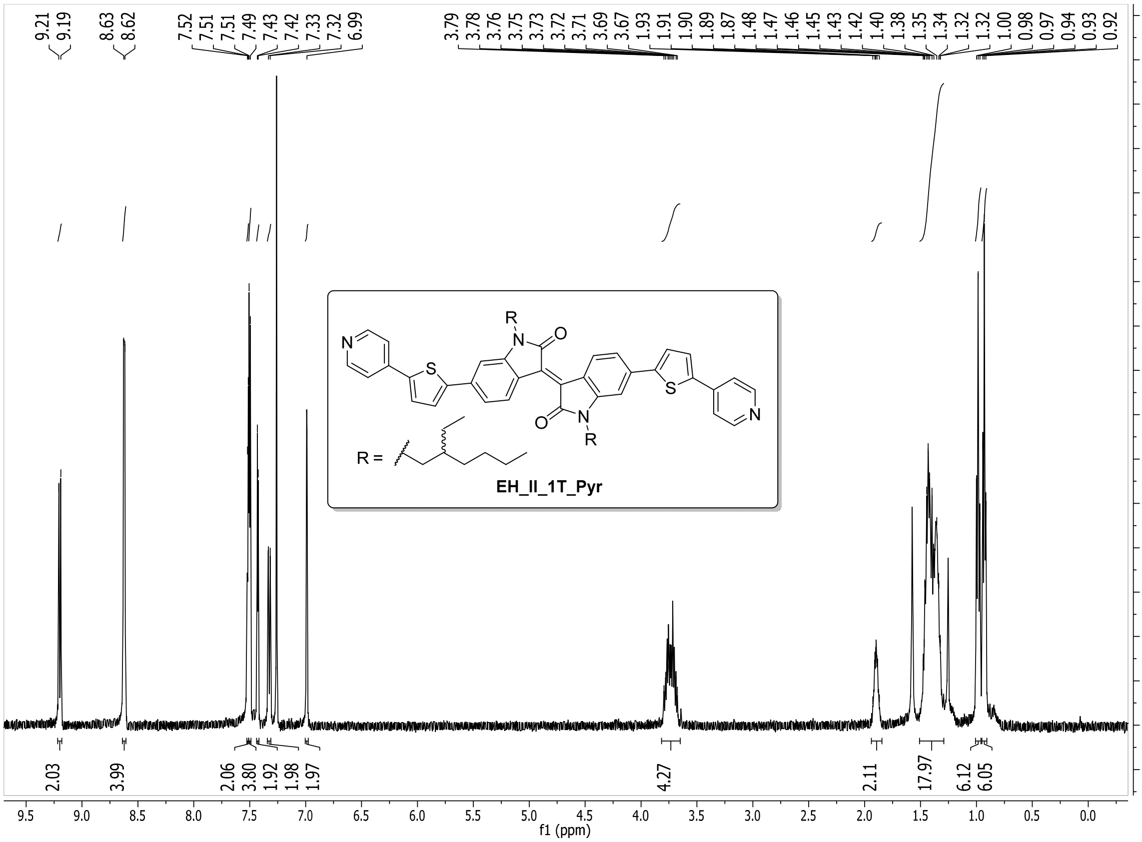

161.5
150.6
141.9
141.5
140.5
139.3
137.8
136.9
128.9
126.5
126.2
125.4
119.5
108.7
46.1
39.5
30.5
28.7
23.8
23.3
14.3
10.7
EH_DPP_2T_Pyr
N
S
R
O
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0

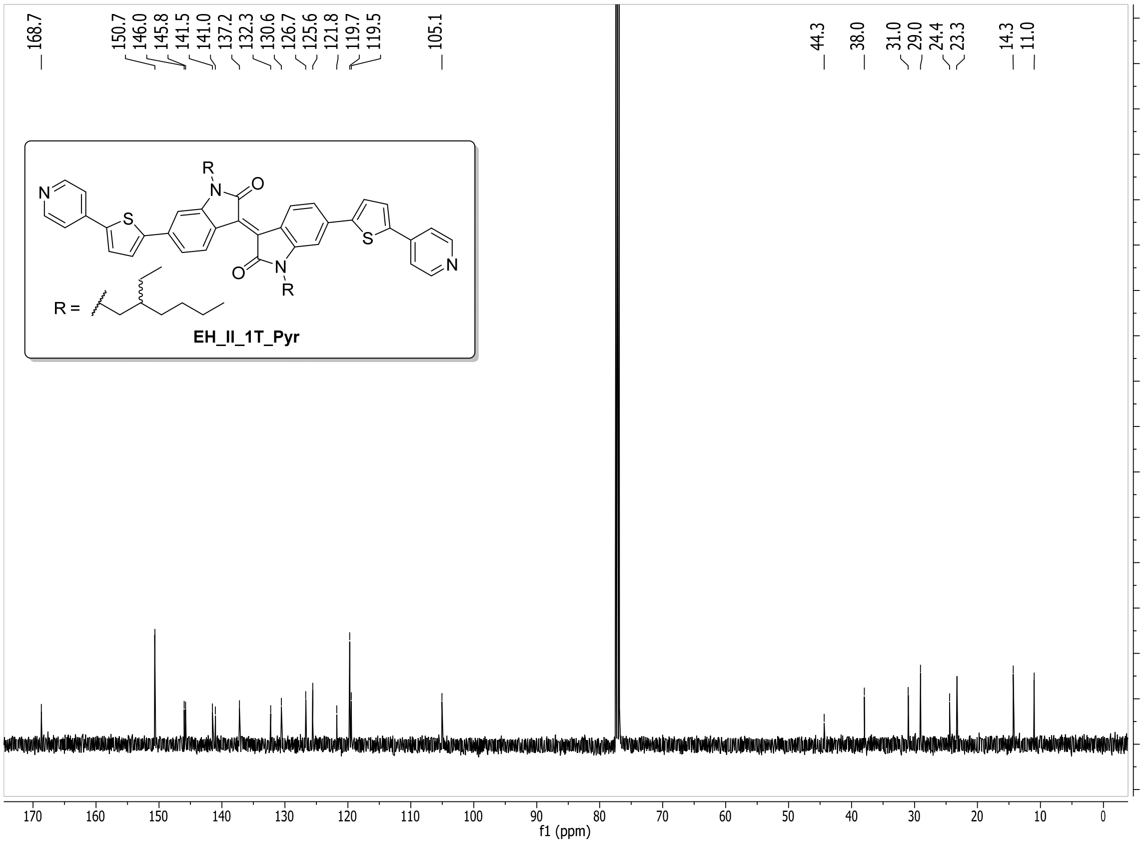


EH_II_2T_Pyr



EH_II_2T_Pyr


9.21
9.19
8.63
8.62
7.52
7.51
7.51
7.49
7.43
7.42
7.33
7.32
6.99
3.79
3.78
3.76
3.75
3.73
3.72
3.71
3.69
3.67
1.93
1.91
1.90
1.89
1.87
1.48
1.47
1.46
1.45
1.43
1.42
1.40
1.38
1.35
1.34
1.32
1.32
1.00
0.98
0.97
0.94
0.93
0.92
R
N
O
S
N
O
N
R
S
N
R =
EH_II_1T_Pyr
2.03
3.99
2.06
3.80
1.92
1.98
1.97
4.27
2.11
17.97
6.12
6.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5


168.7
150.7
146.0
145.8
141.5
141.0
137.2
132.3
130.6
126.7
125.6
121.8
119.7
119.5
105.1
44.3
38.0
31.0
29.0
24.4
23.3
14.3
11.0
R
N
O
S
N
O
N
R
S
N
R =
EH_II_1T_Pyr
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

References:

1. M. J. Frisch, G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. Cheeseman, G. Scalmani, V. Barone,B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, H. A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada and D. Fox, *Gaussian 09 Revision A.1.* Gaussian Inc., Wallingford, CT, 2009.
2. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics,* 1996, **14**, 33.
3. J. Mei, K. R. Graham, R. Stalder and J. R. Reynolds, *Org. Lett.,* 2010, **12**, 660.
4. R. B. Zerdan, N. T. Shewmon, Y. Zhu, J. P. Mudrick, K. J. Chesney, J. Xue and R. K. Castellano, *Adv. Funct. Mater.,* 2014, **24**, 5993.
5. A. B. Tamayo, M. Tantiwiwat, B. Walker and T. Q. Nguyen, *J. Phys. Chem. C,* 2008, **112,** 15543.
6. J. R. Matthews, W. Niu, A. Tandia, A. L. Wallace, J. Hu,W. Y. Lee, G. Giri, S. C. B. Mannsfeld, Y. Xie, S. Cai, H. H. Fong, Z. Bao and M.He, *Chem. Mater.,* 2013, **25**, 782.
7. J. Wilson, J. S. Dal Williams, C. Petkovsek, P. Reves, J. W. Jurss, N. I. Hammer, G. S. Tschumper and D. L. Watkins, *RSC Adv.,* 2015, **5**, 82544.
8. E. C. Constable, C. E. Housecroft, M. Neuburger and C. X. Schmitt, *Polyhedron,* 2006, **25**, 1844.
9. A. Abbotto, S. Bradamante, A. Facchetti and G. A. Pagani, *J. Org. Chem.,* 1997, **62**, 5755.
10. Y. Yang, R. Wu, X. Wang, X. Xu, Z. Li, K.Li and Q. Peng, *Chem. Commun.,* 2014, **50**, 439.