

Supplementary Information

Synthesis and Optoelectronic Properties of Benzodithiophene-Based Conjugated Polymers with Hydrogen Bonding Nucleobase Side Chain Functionality

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Materials and Methods

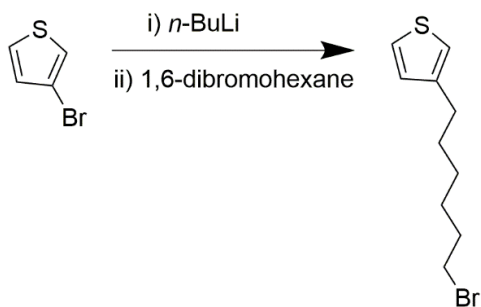
All chemicals and solvents were purchased from Sigma-Aldrich or Fisher Scientific and used as received unless otherwise stated. Tetrakis(triphenylphosphine) palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) was purchased from Strem Chemicals and used without additional purification. (4,8-Didodecylbenzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**BDT_d**) and ((4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**BDT_{eho}**) were purchased from Solarmer Energy Inc. Toluene, THF and *N,N*-dimethylformamide (DMF) were purified using an Innovative Technologies MD-5 Solvent Purification System and degassed prior to use. *N*-bromosuccinimide was recrystallized from hot (distilled) water prior to use. All synthesized materials were purified via column chromatography using 60 Å silica gel (40-63 μm, Sorbent Technologies).

^{13}C and ^1H NMR spectra of synthesized molecules and polymers were acquired using a Varian Mercury Vx 300 MHz NMR at room temperature using 15–20 mg mL⁻¹ solutions in CDCl₃. Chemical shifts are reported in units of δ (ppm) and referenced to the residual solvent peak. A JEOL AccuTOF DART mass spectrometer was used to analyze samples that were constituted at ~1 mg mL⁻¹ using toluene as the solvent. The average molecular weight and dispersity of synthesized polymers were determined by size exclusion chromatography using an Agilent 1260 Infinity II GPC system. Macromolecular characteristics reported are based on universal calibration using polystyrene standards. The system contained two Agilent PLgel Mixed-D columns (7.5 × 300 mm) in sequence, and detectors include an Optilab® T-rEX™ RI detector, a Wyatt Dawn® Helios® Multi-Angle Light Scattering Detector, and a ViscoStar® III viscometer. Samples were dissolved in THF (~ 5 mg/mL) and passed through a 0.2 μm PTFE filter prior to analysis. The flow rate of the THF mobile phase was set at 1 mL/min.

A Nicolet iS50 FT-IR Spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector was used to measure the absorption spectrum of dry powder samples in the mid-IR region (4000-400 cm⁻¹) in attenuated total reflection (ATR) mode.

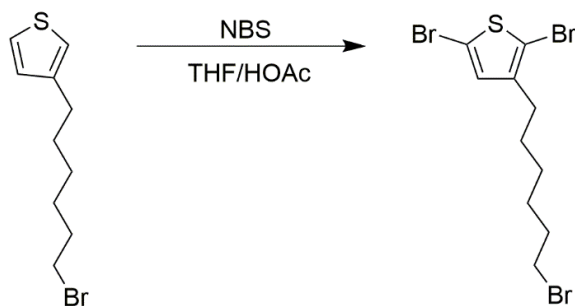
Synthesis of Nucleobase Containing Monomers

3-(6-bromohexyl)thiophene was synthesized following published procedures:¹



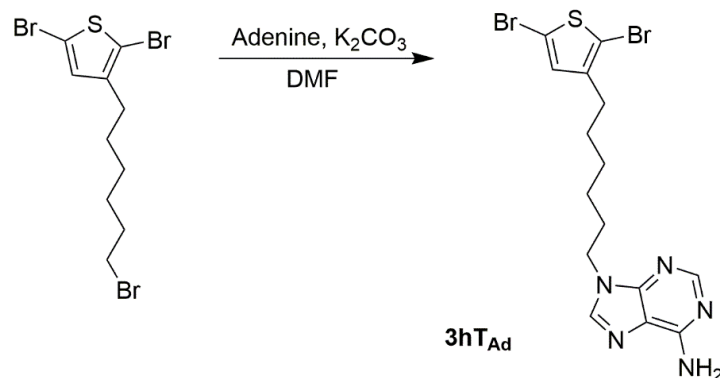
An oven-dried 3-neck flask sealed with rubber septa was cooled under vacuum to room temperature and refilled with Ar gas. 50 mL of dry, degassed hexane was transferred to the 3-neck flask via cannula and cooled to -78 °C using a dry ice/isopropanol bath, after which time 4.0 mL of *n*-butyllithium solution (2.5 M in hexane, 10 mmol) was added dropwise to the reaction flask over 30 minutes. Then, 5 mL of dry and degassed THF was added and the mixture stirred at -78 °C for 30 minutes before dropwise addition of 1.0 mL of 3-bromothiophene (10.65 mmol). This mixture was stirred for 1 h, and after that time, an excess of 1,6-dibromohexane (16 mL, 106.5 mmol) was added. While stirring, the mixture was allowed to warm to the room temperature by removing the isopropanol bath. After allowing the reaction to proceed overnight, the reaction was quenched by adding 100 mL water. The product was extracted using 100 mL of diethyl ether, and the aqueous phase separated using an extraction funnel. The organic phase was dried over MgSO₄ and then filtered and concentrated via rotary evaporation. Excess 1,6-dibromohexane was removed by vacuum distillation at 65 °C (30 mtorr) and the product was purified by silica gel column chromatography using hexanes as the mobile phase. The product was recovered as a colorless oil (70% yield based on isolated product). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.24 (dd, 1H, *J* = 4.9, 3.0 Hz), 6.94 – 6.90 (m, 2H), 3.41 (t, 2H, *J* = 6.7 Hz), 2.64 (t, 2H, *J* = 7.5 Hz), 1.90 – 1.83 (m, 2H), 1.68 – 1.61 (m, 2H), 1.51 – 1.44 (m, 2H), 1.40 – 1.33 (m, 2H). ¹³C-NMR (300 MHz, CDCl₃) δ (ppm): 142.9, 128.2, 125.2, 119.9, 33.9, 32.7, 30.3, 30.1, 28.4, 28.0. AccuTOF DART: calc'd [M+H⁺]: 247.0156, found [M+H⁺] 247.0155.

2,5-dibromo-3-(6-bromohexyl)thiophene was synthesized following procedures described by Green et al.¹



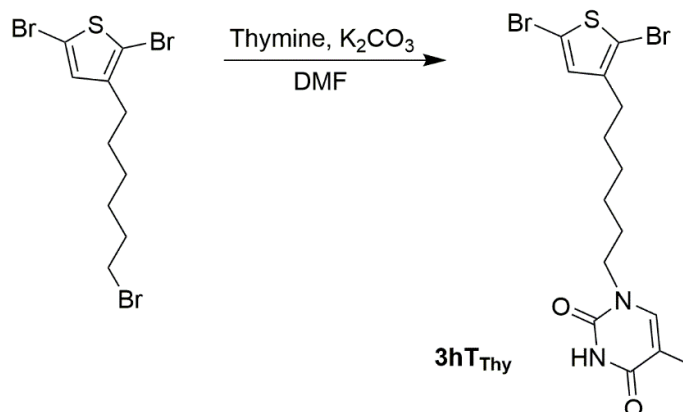
An oven-dried 3-neck round bottom flask was cooled to room temperature under vacuum. To ensure an inert environment, the flask was evacuated and then refilled with Ar 3 times. 25 mL of dry and degassed THF and 25 mL of glacial acetic acid were added via syringe. 3-(6-bromohexyl) thiophene (0.985 g, 4 mmol, 1 equiv.) was added to the THF/acetic acid mixture and stirred for 30 min at room temperature. Under positive argon pressure, 1.495 g of freshly recrystallized NBS (8.4 mmol, 2.1 equiv.) was added in one portion to the mixture and the flask covered from light. The resulting mixture was stirred for 3 h at room temperature. After this time, the reaction was quenched by adding a saturated solution of sodium bicarbonate. The product was extracted to the organic phase with 100 mL of diethyl ether and the aqueous phase was discarded. The organic phase was washed with brine, isolated, then dried over MgSO₄. The MgSO₄ was removed by filtration and the product was concentrated via rotary evaporation. Silica gel column chromatography using hexanes as the mobile phase was used to purify the product, which was collected as a colorless oil. (75% yield based on the isolated product.) ¹H NMR (300 MHz, CDCl₃), δ (ppm): 6.77 (s, 1H), 3.40 (t, 2H, *J* = 6.8 Hz), 2.52 (t, 2H, *J* = 7.6 Hz), 1.91 – 1.81 (m, 2H) 1.62 – 1.52 (m, 2H), 1.50 – 1.40 (m, 2H) 1.40 – 1.30 (m, 2H). ¹³C-NMR (300 MHz, CDCl₃) δ (ppm): 142.6, 130.9, 110.5, 108.1, 33.8, 32.6, 29.34, 29.29, 28.2, 27.9. AccuTOF DART: calc'd [M+H⁺]: 404.8346 Found: 404.8312.

Synthesis of adenine-containing dibromo thiophene monomer, **3hT_{Ad}**:



50 mL of dry and degassed DMF was added to a dry 100 mL round bottom flask under positive Ar pressure. Then, 821 mg (2.03 mmol) of 2,5-dibromo-3-(6-bromohexyl)thiophene, 547 mg of adenine (4.05 mmol, 2 equiv.), and 839 mg (6.08 mmol, 3 equiv.) of potassium carbonate were added to the mixture. The mixture was stirred at room temperature for 24 h. After this time, the solvent was removed under high vacuum at 50°C. Then, the product was extracted using 100 mL of dichloromethane (DCM) and washed using water and brine solutions. Silica gel column chromatography was used to recover the product, using 5% MeOH in DCM as the mobile phase. The product of N9 alkylation was collected as the major product with 55% yield (based on isolated product) as a white solid. 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35 (s, 1H), 7.77 (s, 1H), 6.72 (s, 1H), 6.13 (s, 2H) 4.17 (t, 2H, $J = 7.2$ Hz), 2.46 (t, 2H, $J=7.5$ Hz), 1.96 – 1.81 (m, 2H) 1.58 – 1.44 (m, 2H), 1.40 – 1.28 (m, 4H). ^{13}C -NMR (300 MHz, $CDCl_3$) δ (ppm): 155.6, 152.9, 150.1, 142.5, 140.3, 130.8, 119.7, 110.5, 108.1, 43.9, 30.0, 29.3, 29.2, 28.4, 26.4. AccuTOF DART: calc'd $[M+H^+]$: 459.9629 Found: 459.9484.

Synthesis of thymine-containing dibromo thiophene monomer, **3hT_{Thy}**:



50 mL of dry and degassed DMF was added to a dry 100 mL round bottom flask under positive Ar pressure. Then, 619 mg (1.53 mmol, 1 equiv.) of 2,5-dibromo-3-(6-bromohexyl)-thiophene, 385 mg of thymine (3.06 mmol, 2 equiv.), and 633 mg (4.59 mmol, 3 equiv.) of potassium carbonate were added to the mixture. The mixture was stirred at room temperature for 24 h. After this time, the solvent was removed under high vacuum at 50°C. Then, the product was extracted using 100 mL of DCM and washed with water and brine solutions. Silica gel column chromatography was used to recover the product, using 3% MeOH in DCM as the mobile phase. The product of N1 alkylation was collected as a white solid with a 62% yield based on isolated product. 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.69 (s, 1H) 6.95 (s, 1H), 6.74 (s, 1H), 3.66 (t, 2H, $J = 7.2$ Hz), 2.48 (t, 2H, $J=7.5$ Hz), 1.90 (s, 3H) 1.68 – 1.62 (m, 2H), 1.56 – 1.49 (m, 2H) 1.35 – 1.31 (m, 4H). ^{13}C -NMR (300 MHz, $CDCl_3$) δ (ppm): 164.6, 151.1, 142.6, 140.4, 130.9, 110.6, 110.5, 108.1, 48.4, 29.3, 29.0, 28.5, 26.2, 12.3. AccuTOF DART: calc'd $[M+H^+]$: 450.9513 Found: 450.9527.

NMR Spectra of Small Molecules

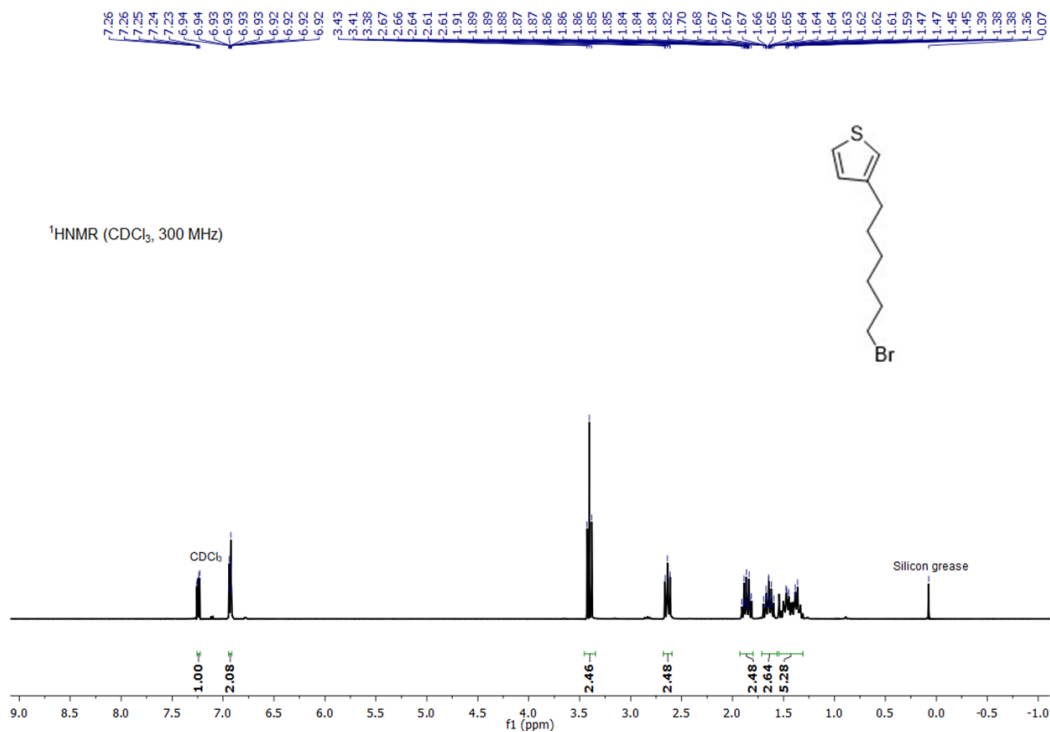


Figure S1. ¹H NMR spectrum of 3-(6-bromohexyl) thiophene (CDCl₃, 25 °C).

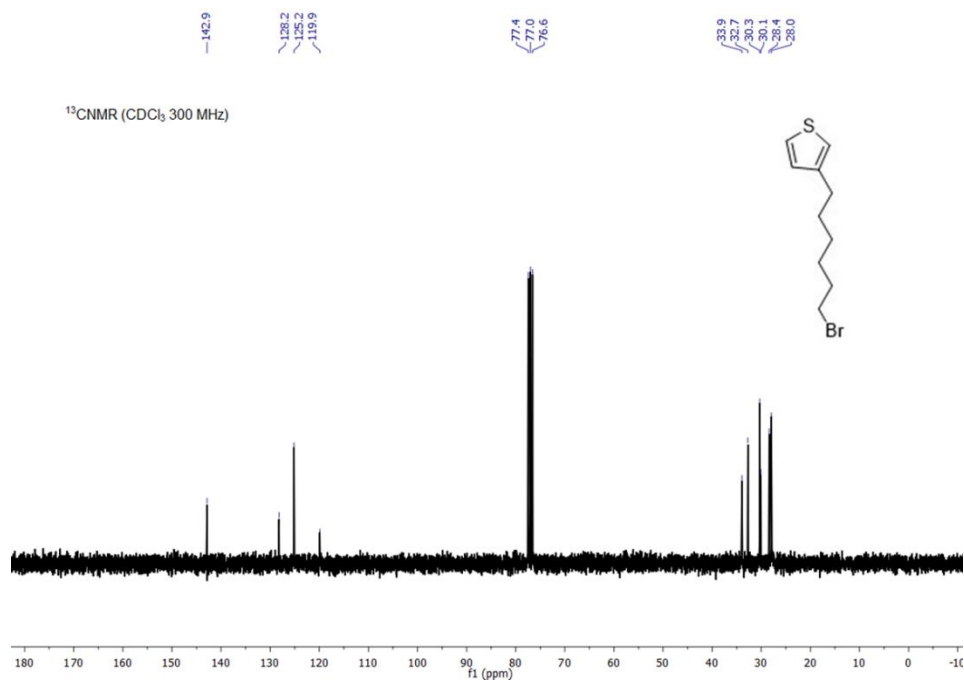


Figure S2. ¹³C NMR spectrum of 3-(6-bromohexyl) thiophene (CDCl₃, 25 °C).

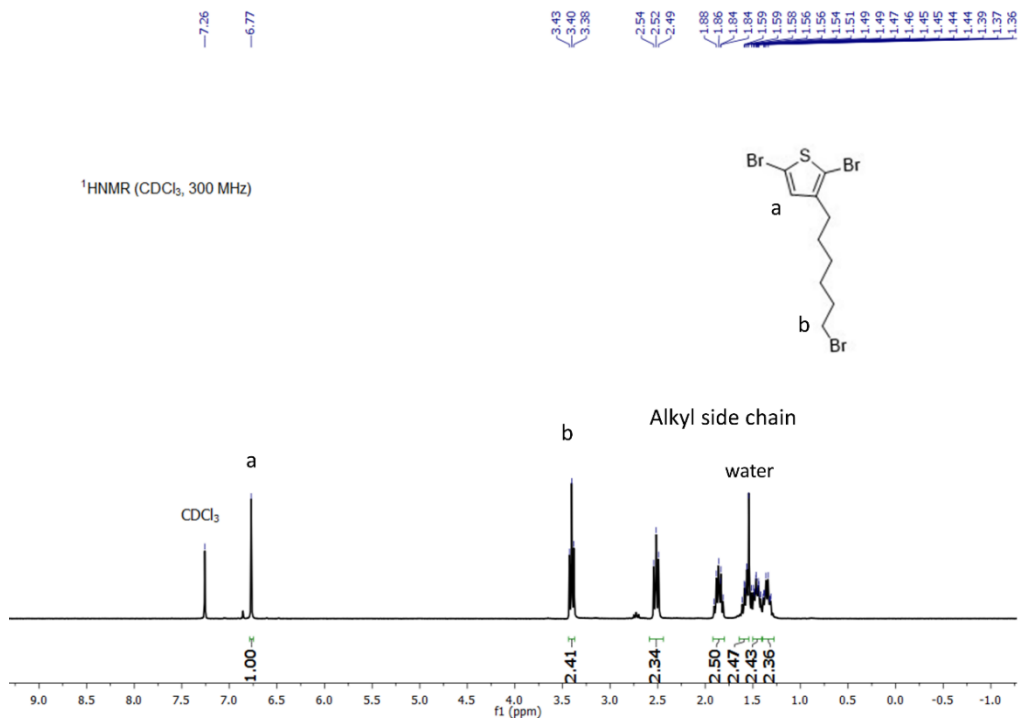


Figure S3. ¹H NMR spectrum of 2,5-dibromo-3-(6-bromohexyl) thiophene (CDCl₃, 25 °C).

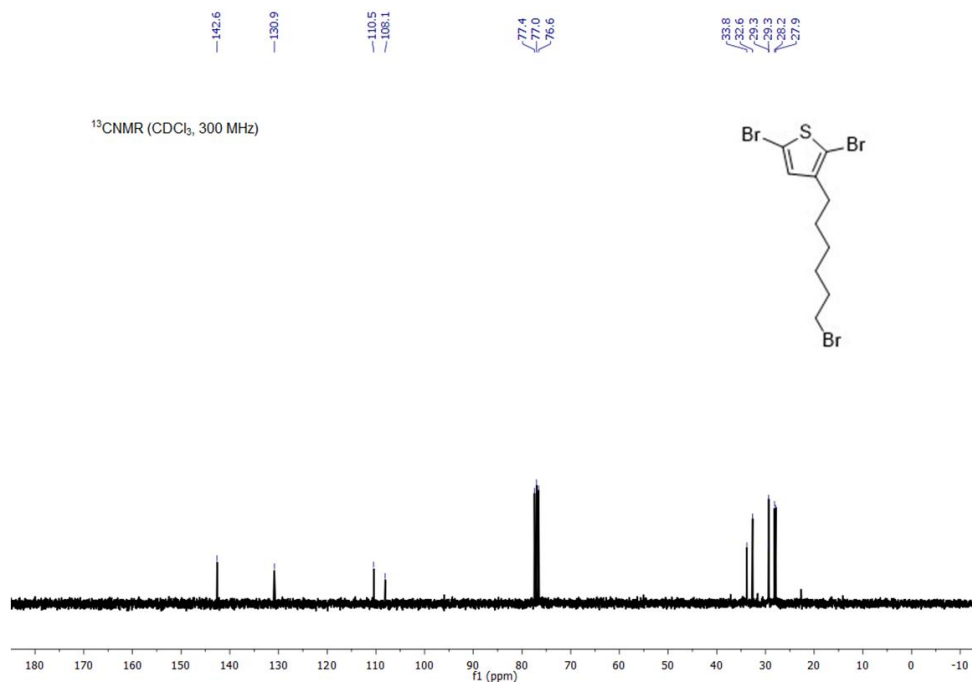


Figure S4. ¹³C NMR spectrum of 2,5-dibromo-3-(6-bromohexyl) thiophene (CDCl₃, 25 °C).

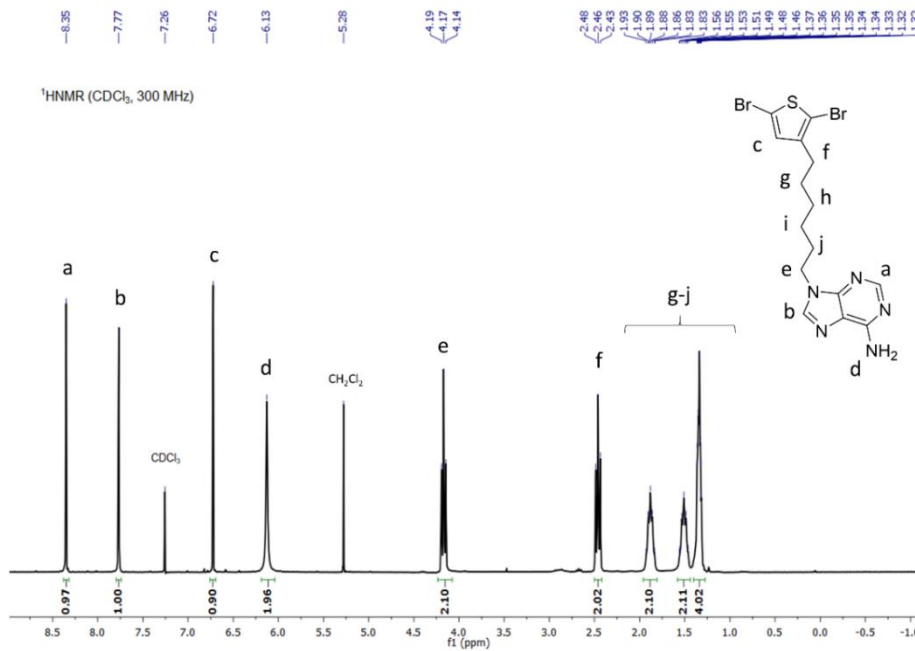


Figure S5. ¹H NMR spectrum of adenine containing dibromo thiophene monomer, **3hTAd** (CDCl₃, 25 °C).

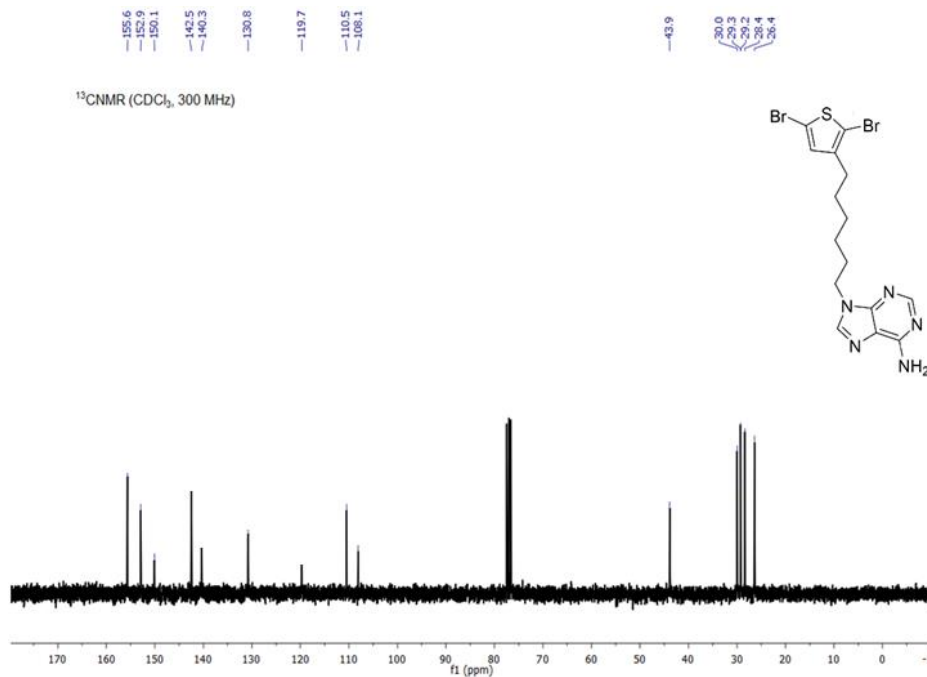


Figure S6. ¹³C NMR spectrum of adenine containing dibromo thiophene monomer, **3hTAd** (CDCl₃, 25 °C).

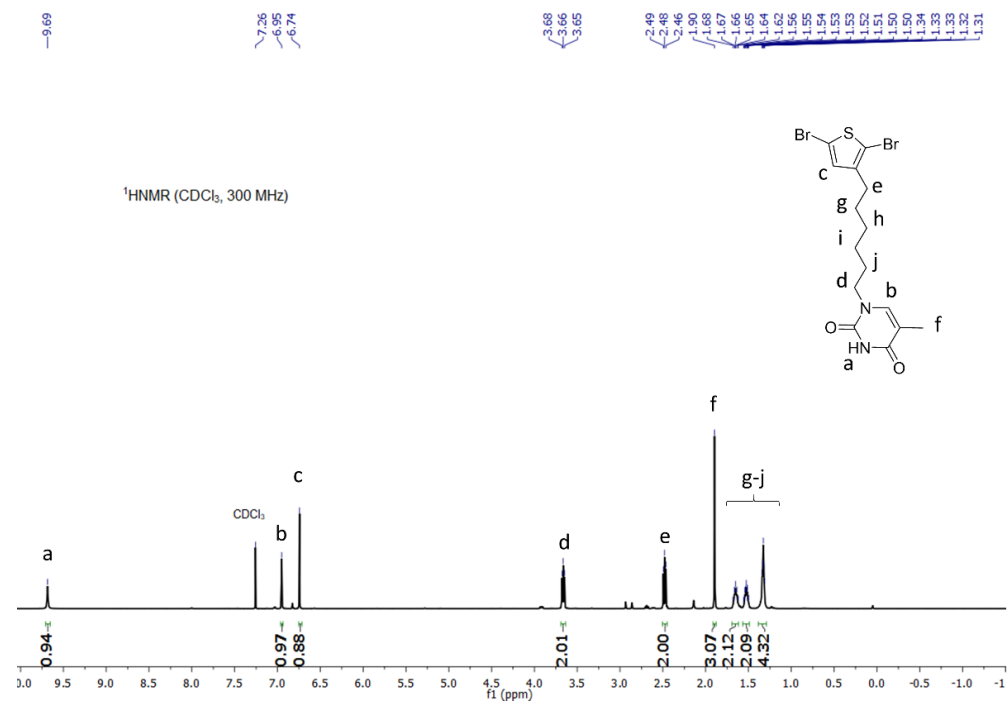


Figure S7. ¹H NMR spectrum of thymine containing dibromo thiophene monomer, **3hT_{Thy}** (CDCl₃, 25 °C).

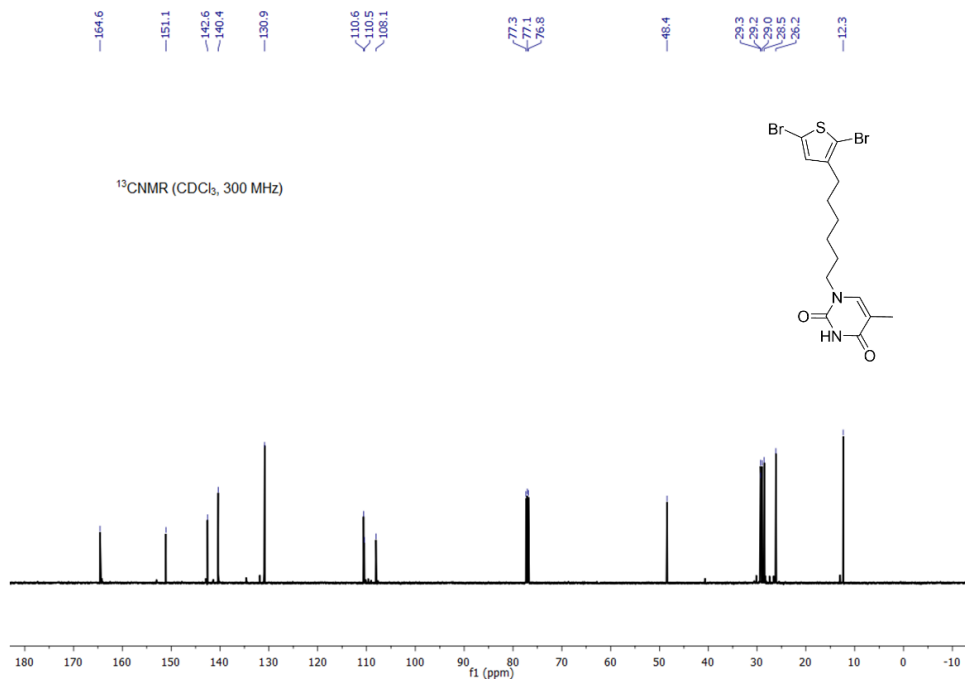


Figure S8. ¹³C NMR spectrum of thymine containing dibromo thiophene monomer, **3hT_{Thy}** (CDCl₃, 25 °C).

Synthesis of $\text{BDT}_R\text{-3hT}_X$ Alternating Copolymers

General Stille Polymerization Conditions. Dibromo thiophene monomer ($\mathbf{3hT}_{Ad}$, $\mathbf{3hT}_{Thy}$, or $\mathbf{3hT}$; 1 equiv., 1 mmol), bistannylbenzodithiophene (\mathbf{BDT}_d , or \mathbf{BDT}_{eho} ; 1 equiv., 1mmol), and Pd catalyst ($\text{Pd}(\text{PPh}_3)_4$, 0.1 mmol, 10 mol%) were added to a dry 50 mL round bottom flask while it was under positive Ar pressure and sealed with rubber septa. Dry DMF (10 mL) was then transferred via cannula to the reaction flask and the reaction mixture was heated at 100 °C for 24 h. After the prescribed time, the reaction mixture was cooled to room temperature and the polymer was precipitated into methanol. The precipitate was washed with methanol and acetone in a Soxhlet thimble. The product was then extracted with chloroform and concentrated (~10 mL solution) in rotary evaporator. Then, 1,4-dioxane (~5 mL) was added and chloroform was removed under reduced pressure yielding a polymer solution in dioxane (wet solvent exchange). The solid was recovered after freeze-drying from dioxane solution. Molecular weight data (relative to polystyrene standards) for these polymers are presented in Table 1 of the *Article*.

$\text{BDT}_d\text{-3hT}_{Ad}$: Dark red solid, 55 % yield, $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 8.35, 7.76, 7.52, 7.48, 7.21, 4.17, 3.14, 2.92, 1.89 – 1.60, 1.51 – 1.35, 0.89 – 0.76.

$\text{BDT}_d\text{-3hT}_{Thy}$: Red solid, 88 % yield, $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.46, 7.22, 6.92, 3.67, 3.16, 2.94, 1.94 – 1.58, 1.56 – 1.15, 0.91 – 0.80.

$\text{BDT}_{eho}\text{-3hT}_{Ad}$: Dark red solid, 64 % yield, $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 8.26, 8.17, 7.82, 7.50, 7.16, 4.21, 3.36, 2.90, 1.90 – 1.53, 1.51 – 1.27, 1.12 – 0.81.

$\text{BDT}_{eho}\text{-3hT}_{Thy}$: Dark red solid, 85 % yield, $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.51, 7.18, 6.91, 4.22, 3.64, 2.93, 1.90 – 1.54, 1.48 – 1.18, 1.11 – 0.74.

$\text{BDT}_d\text{-3hT}$: Red solid, 53 % yield, $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.44, 7.23, 3.12, 2.91, 1.97 – 1.66, 1.53 – 1.21, 1.01 – 0.74.

$\text{BDT}_{eho}\text{-3hT}$: Light red solid, 79 % yield, $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.52, 7.20, 6.90, 4.19, 2.90, 1.86 – 1.61, 1.59 – 1.37, 1.18 – 0.86.

Solvent Transfer Method

Nucleobase functionalized copolymers isolated from chloroform solution following Soxhlet extraction could not be redissolved in common organic solvents, even at elevated temperatures, if they were rotovapped to complete dryness. This proved to be true for chloroform, THF, DCM, DMF, DMAc, acetonitrile, benzene, chlorobenzene, and dioxane, both at room temperature and elevated temperatures (up to the reflux temperature). These outcomes, along with the acknowledged importance of solution processability, led us to develop a novel solvent transfer method for these strongly aggregating, marginally-soluble conjugated polymers. As alluded to in the *Article*, this approach is inspired by colloidal processing methods. Complete and slow removal of solvent results in irreversible aggregation and insolubility. However, the sequential addition of a solvent with boiling point that is higher than chloroform and selective removal of chloroform enables processable solutions in that desired solvent to be created. Fast freezing of the solution followed by solvent removal via freeze-drying circumvents irreversible aggregation, ostensibly resulting in powders with high void volume rather than a highly packed solid obtained by rotovaping.

An overview of the solvent transfer process used in this work is shown in Figure S9. We chose dioxane as the exchange solvent because it has a relatively high boiling point of 101.1 °C and because its freezing point of 11.8 °C makes it an excellent candidate for freeze drying. Solvent exchange of the copolymers was achieved by sequential additions of dioxane as chloroform was removed by rotary evaporation. Once the solvents were exchanged, purified polymer was isolated by freeze drying under vacuum. The freeze-dried powder can be dissolved in most (organic) solvents, whereas if the nucleobase functionalized samples were dried after Soxhlet extraction using chloroform, they would not dissolve in dioxane, rendering it impossible to freeze dry the material. Additionally, it should be noted that solutions can be made directly using this solvent transfer method (without freeze-drying) if the desired solvent has a boiling point higher than the extraction solvent (chloroform).

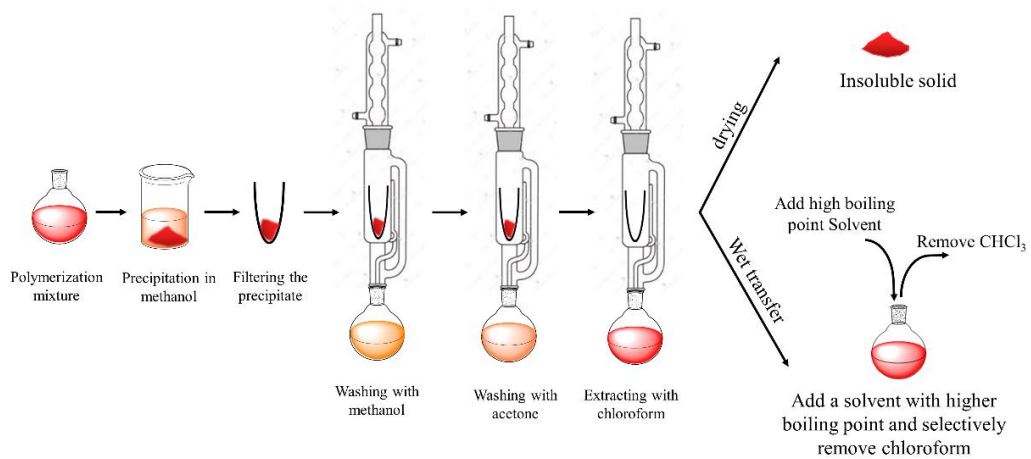


Figure S9. Schematic showing the solvent transfer method used to isolate the purified polymer and make solutions that could be used for film casting.

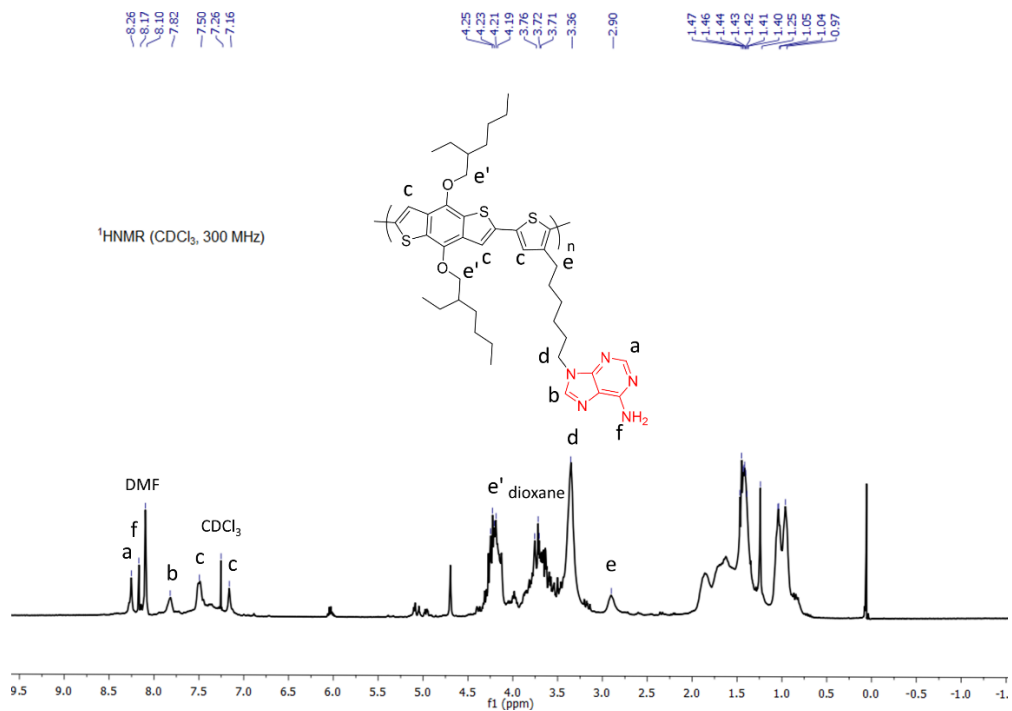


Figure S12. ¹H NMR spectrum of **BDT_{cho}-3hT_{Ad}** (CDCl₃, 25 °C).

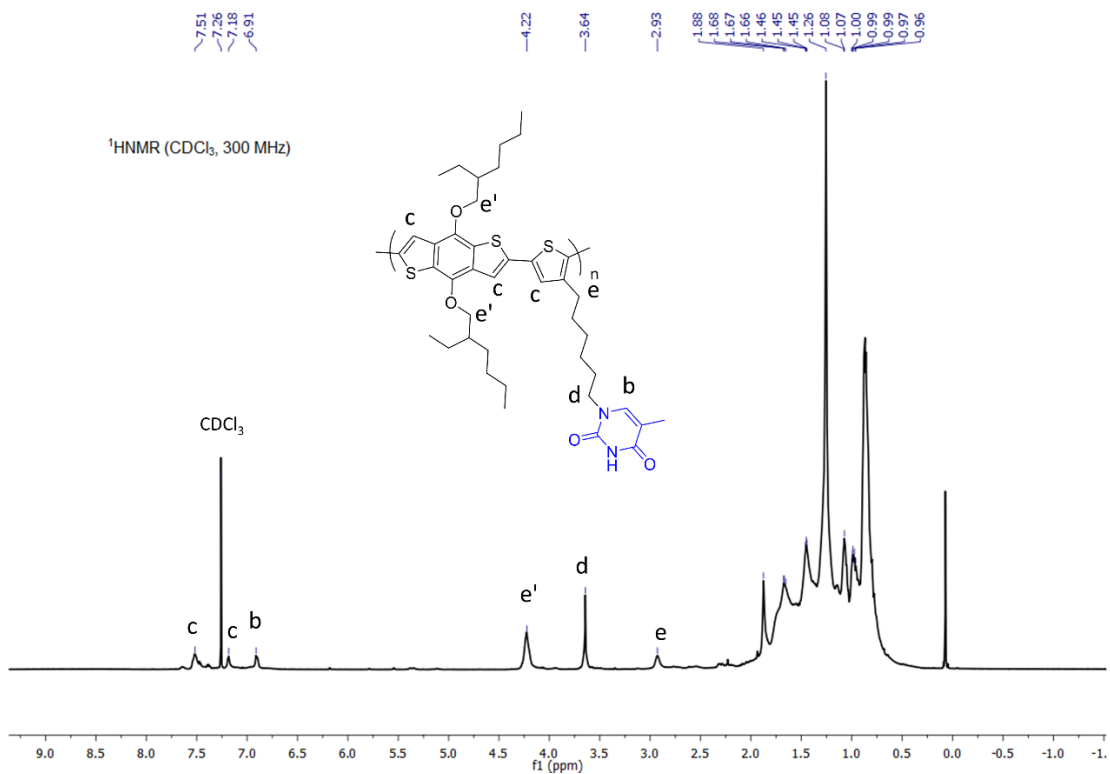


Figure S13. ¹H NMR spectrum of **BDT_{cho}-3hT_{Thy}** (CDCl₃, 25 °C).

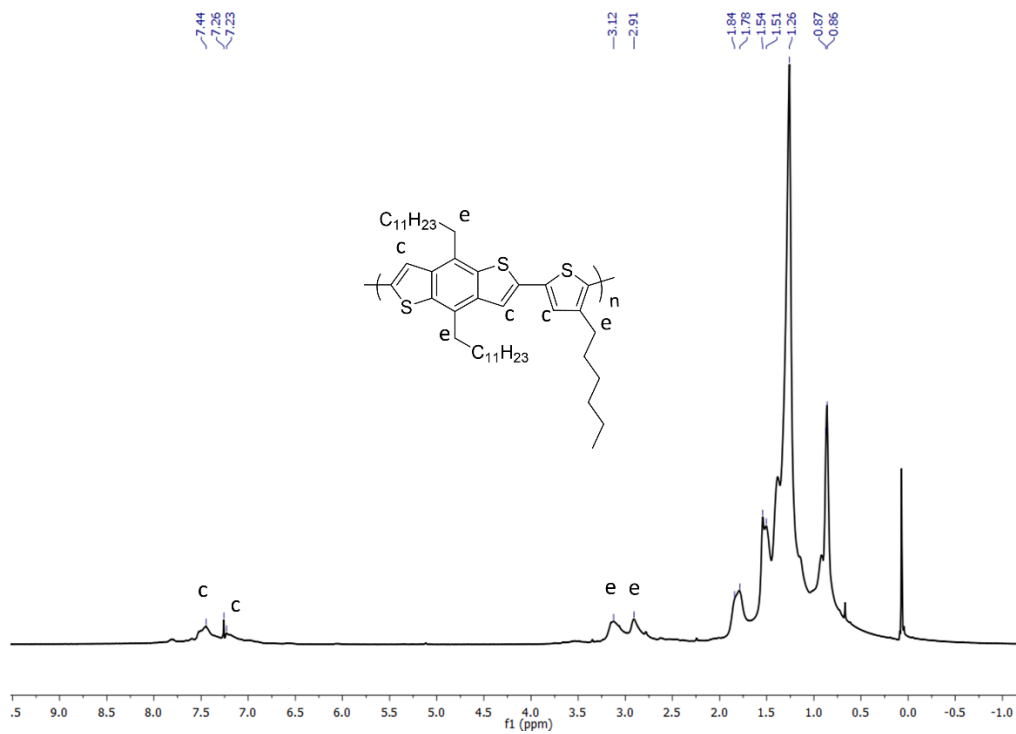


Figure S14. ^1H NMR spectrum of **BDT_a-3hT** (CDCl_3 , 25 °C).

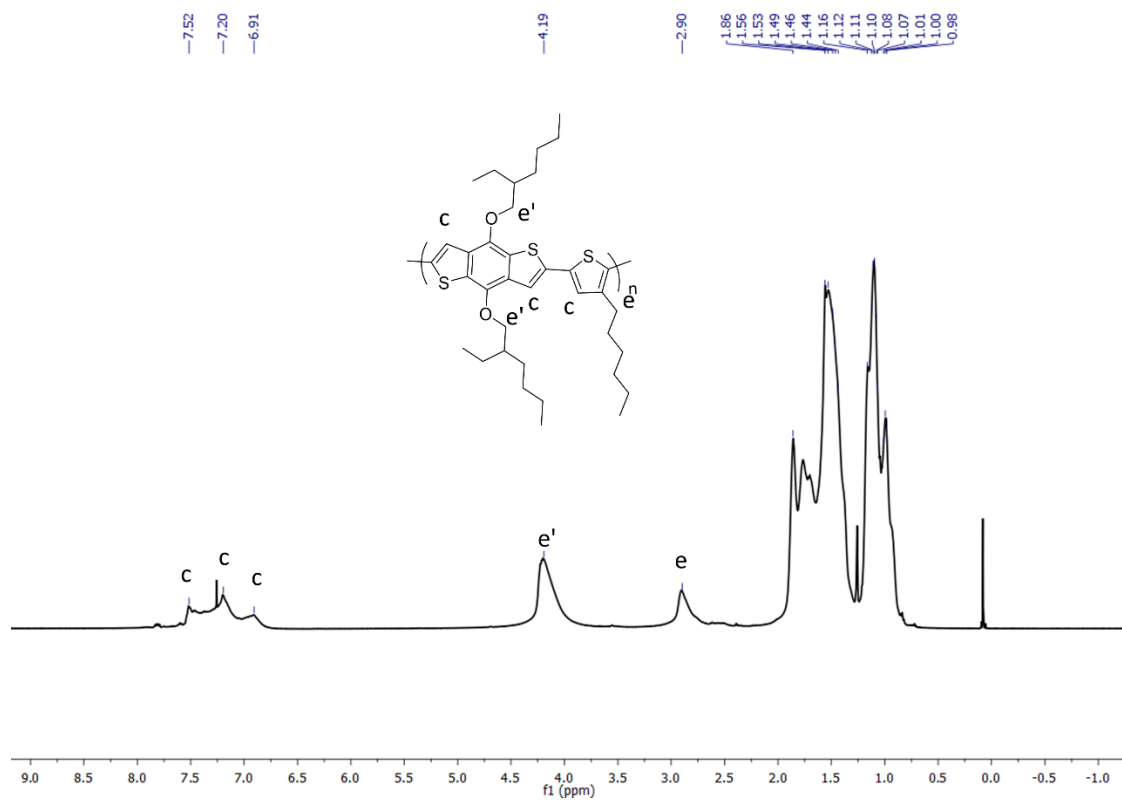


Figure S15. ^1H NMR spectrum of **BDT_{cho}-3hT** (CDCl_3 , 25 °C).

Thermal Characterization of $\text{BDT}_{\text{R}}\text{-3hT}_{\text{X}}$ Copolymers

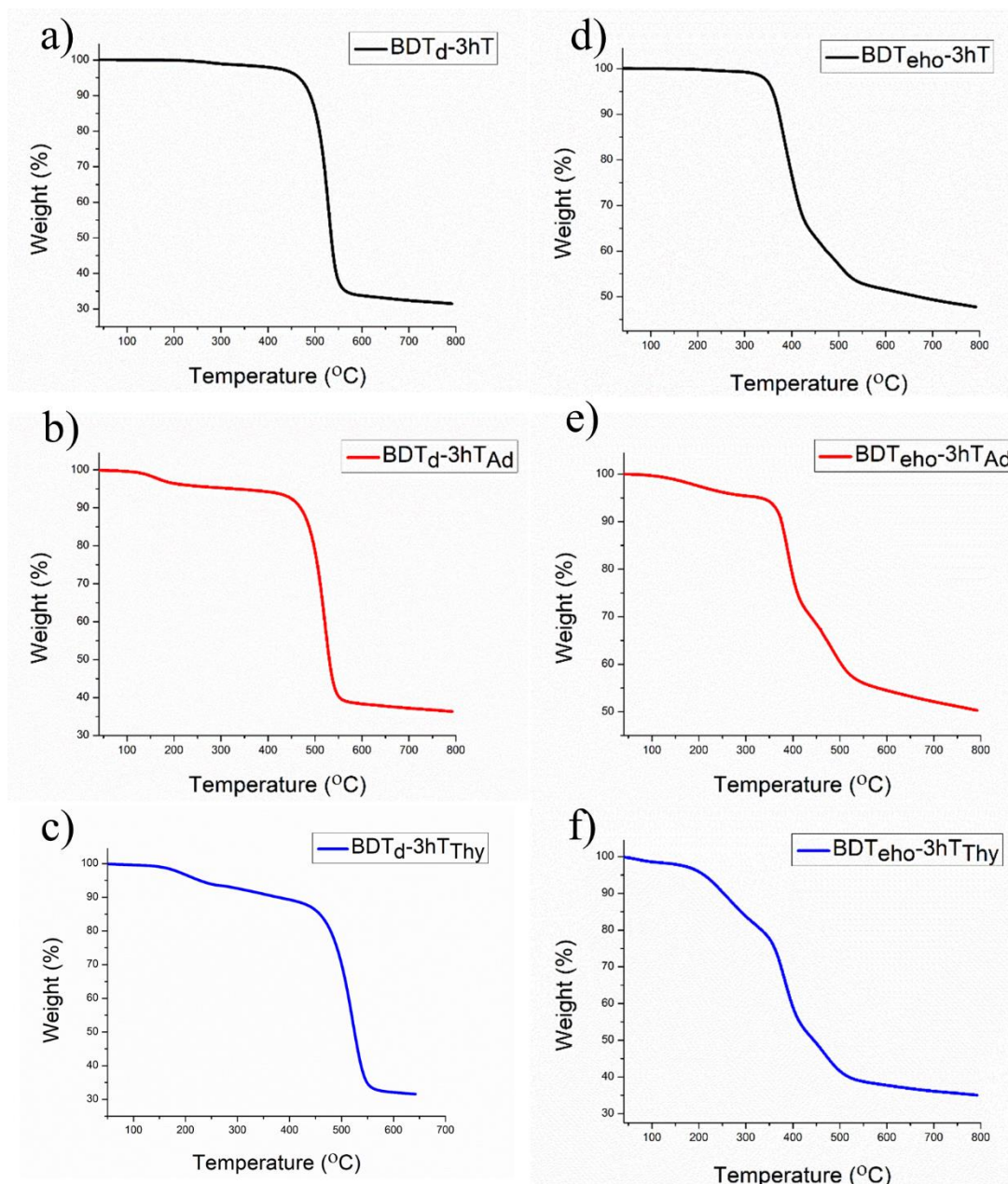


Figure S16. Thermogravimetric analysis of a) $\text{BDT}_{\text{d}}\text{-3hT}$ ($T_{\text{d}} = 465$ °C), b) $\text{BDT}_{\text{d}}\text{-3hT}_{\text{Ad}}$ ($T_{\text{d}} = 317$ °C), c) $\text{BDT}_{\text{d}}\text{-3hT}_{\text{Thy}}$ ($T_{\text{d}} = 230$ °C), d) $\text{BDT}_{\text{eho}}\text{-3hT}$ ($T_{\text{d}} = 360$ °C), e) $\text{BDT}_{\text{eho}}\text{-3hT}_{\text{Ad}}$ ($T_{\text{d}} = 333$ °C), f) $\text{BDT}_{\text{eho}}\text{-3hT}_{\text{Thy}}$ ($T_{\text{d}} = 209$ °C) ramping 40 °C to 800 °C at a rate of 20 °C/min. T_{d} values are based on temperature at 5% weight loss. The minor weight loss observed in f) ~150 °C is most likely due to residual solvent such as DMF (used in polymerization) or dioxane (used for freeze-drying).

DSC studies of alternating copolymers do not show evidence of a distinct glass transition. The lack of an observable T_g by DSC is consistent with various reports of BDT-based conjugated polymers.²⁻⁶

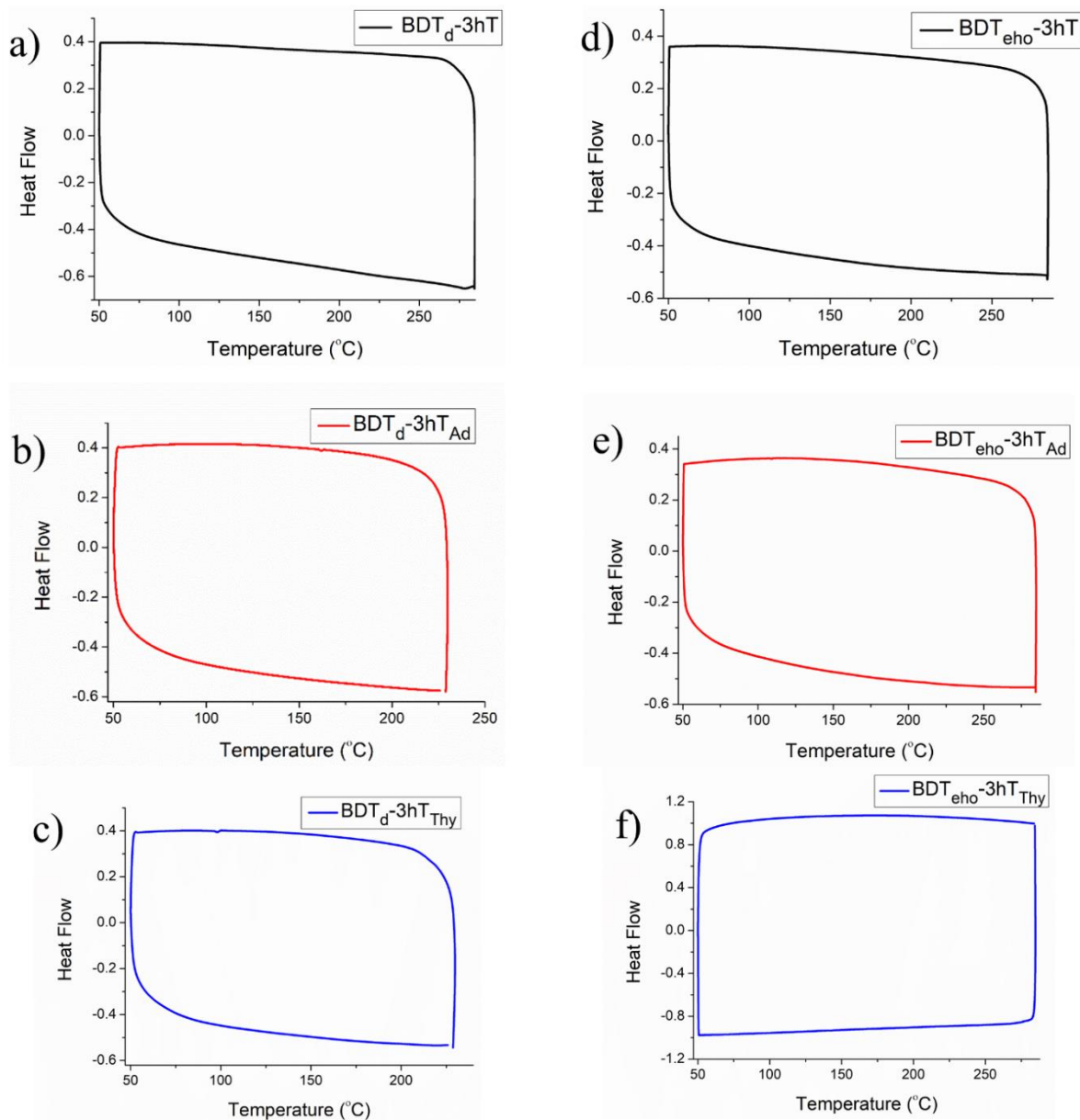


Figure S17. DSC curves (second heating ramp and cooling at the rate of 10 °C/min) of a) **BDT_d-3hT**, b) **BDT_d-3hT_{Ad}**, c) **BDT_d-3hT_{Thy}**, d) **BDT_{eho}-3hT**, e) **BDT_{eho}-3hT_{Ad}**, f) **BDT_{eho}-3hT_{Thy}**.

Host-Guest Hydrogen Bonding Test in Solution

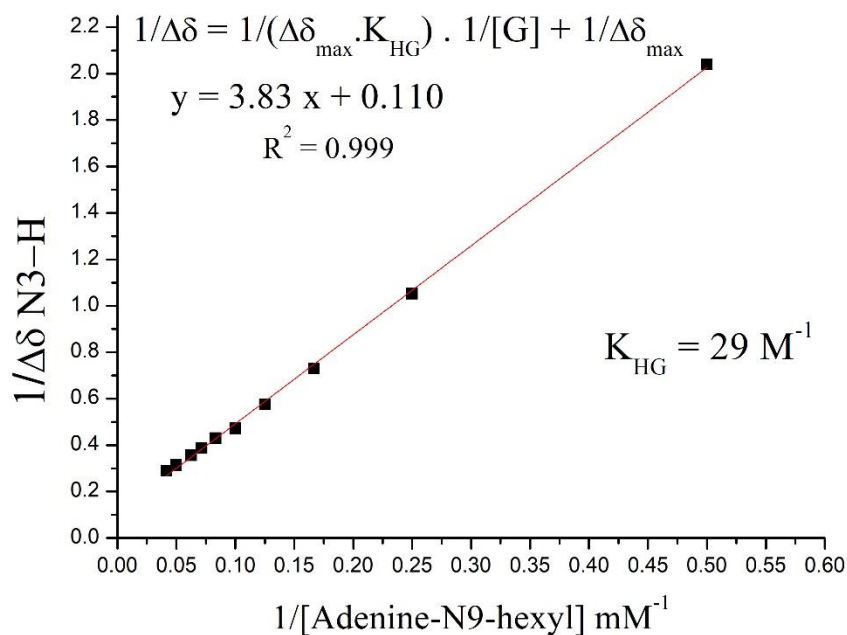




















Figure S18. Dependence of chemical shift of N3-H proton of thymine-N1-hexyl (host) as a function of concentration of adenine-N9-hexyl as the guest molecule. Data are plotted according to the Benesi–Hildebrand model,⁷ which is used to find host-guest association constant, K_{HG} .

Solvent Resistivity Testing

Table S1. Images of thin films of alternating copolymers created by film casting and tested for solvent resistivity. A) **BDT_d-3hT_x** and B) **BDT_{eho}-3hT_x** copolymers.

Sample	As-cast	Rinsed (2x) in chloroform	Sonicated in methanol
BDT_d-3hT			
BDT_d-3hT_{Ad}			
BDT_d-3hT_{Thy}			
BDT_{eho}-3hT			
BDT_{eho}-3hT_{Ad}			
BDT_{eho}-3hT_{Thy}			

UV-vis Absorbance Spectra of Alternating Copolymers (Solutions/Thin Films)

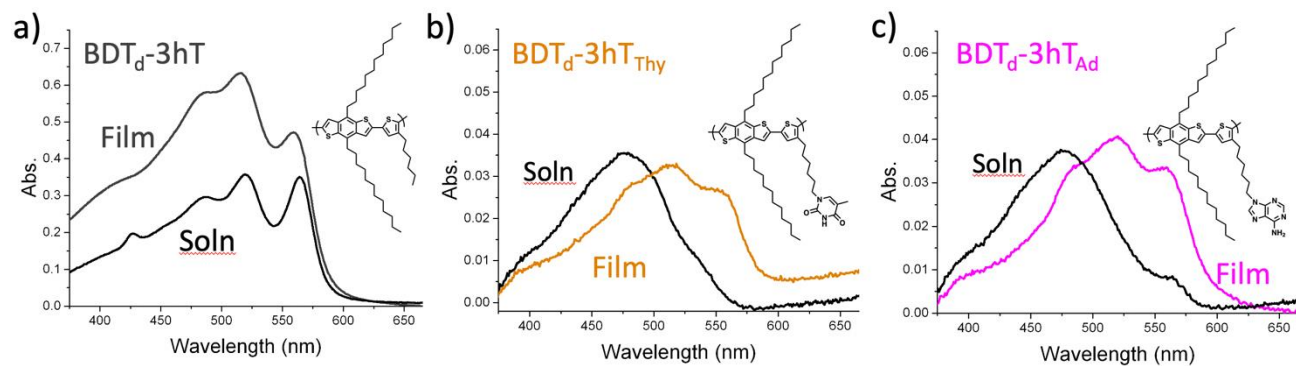
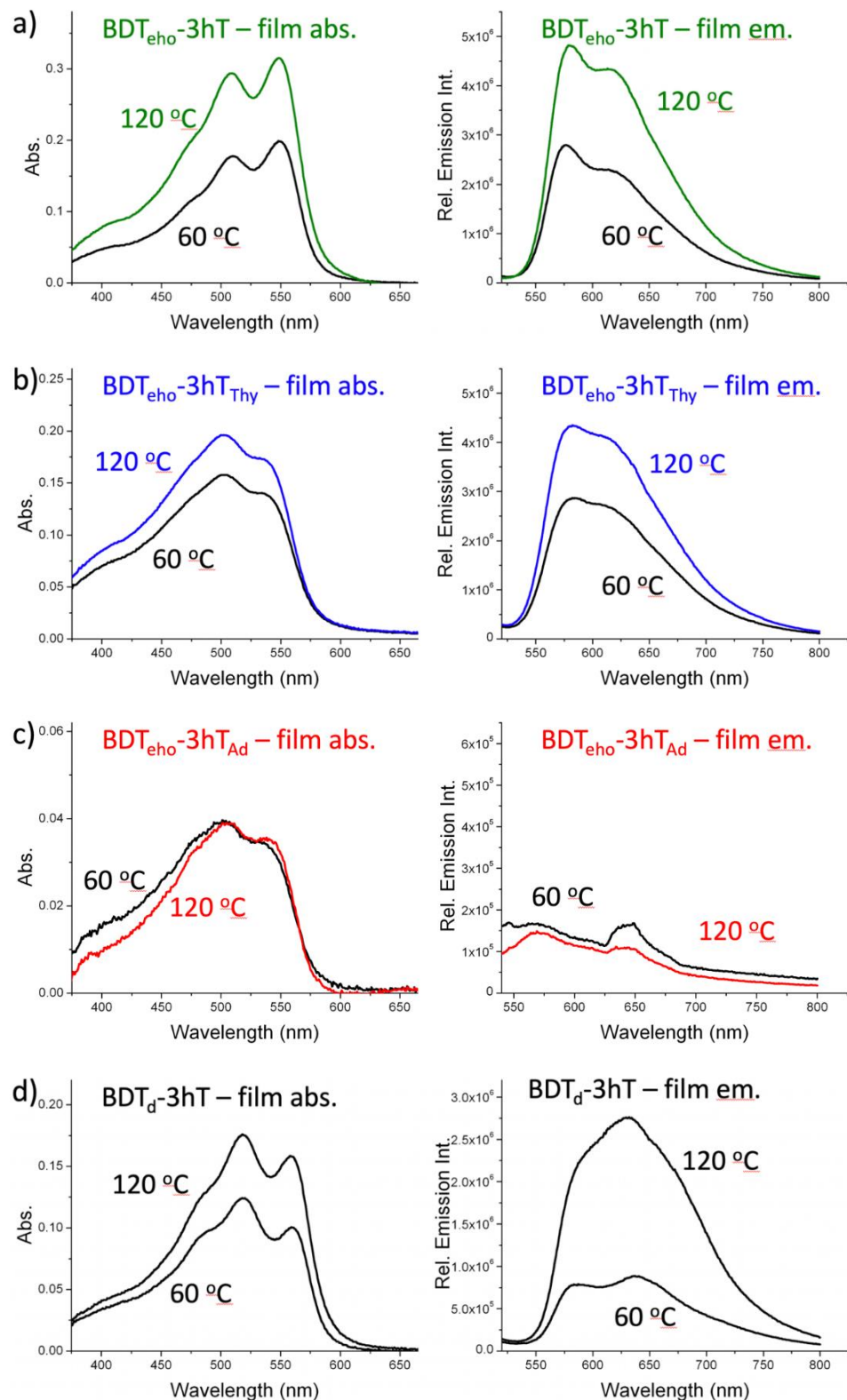


Figure S19. UV-vis absorbance spectra of alternating copolymers in solution (THF) and thin films drop-cast from THF for a) $\text{BDT}_d\text{-3hT}$, b) $\text{BDT}_d\text{-3hT}_{\text{Thy}}$, and c) $\text{BDT}_d\text{-3hT}_{\text{Ad}}$.

UV-vis Absorbance and Emission Spectra of Thin Films Processed at 60 °C and 120 °C



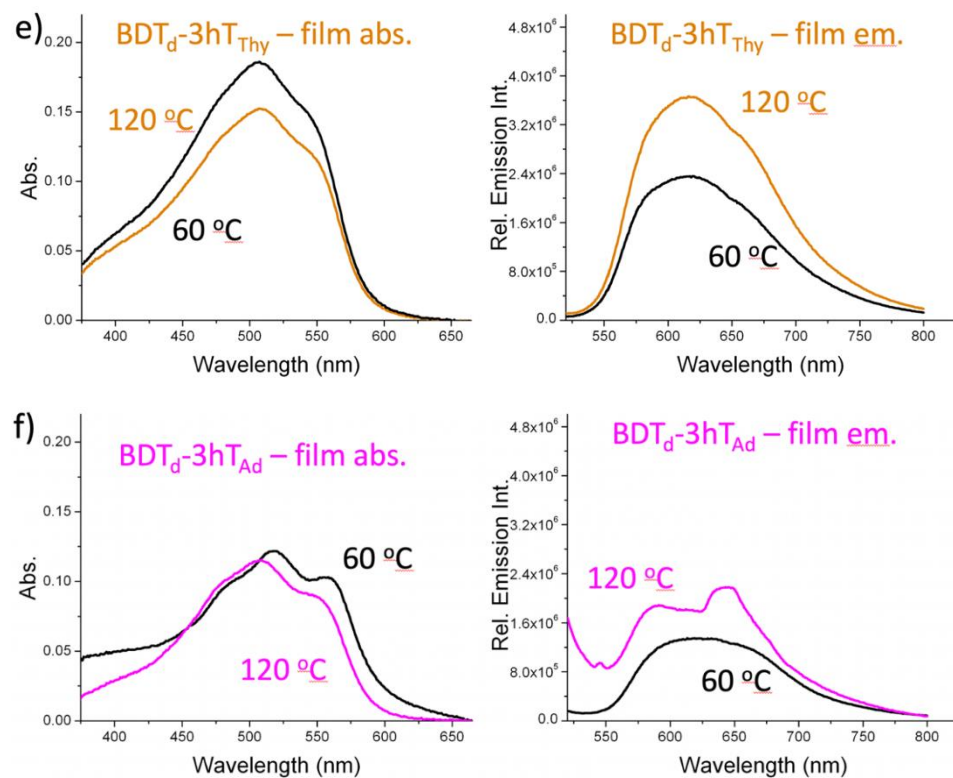


Figure S20. Absorbance and emission spectra of films created by preheating solutions at 60 °C or at 120 °C: a) $\text{BDT}_{\text{eho-3hT}}$, b) $\text{BDT}_{\text{eho-3hT}_{\text{Thy}}}$, c) $\text{BDT}_{\text{eho-3hT}_{\text{Ad}}}$, d) $\text{BDT}_d\text{-3hT}$, e) $\text{BDT}_d\text{-3hT}_{\text{Thy}}$, and f) $\text{BDT}_d\text{-3hT}_{\text{Ad}}$. Note: low film thicknesses or possible fluorescence quenching resulted in low intensity emission spectra for adenine containing polymers $\text{BDT}_{\text{eho-3hT}_{\text{Ad}}}$ and $\text{BDT}_d\text{-3hT}_{\text{Ad}}$.

UV-vis Absorbance Spectra of As-Cast and Annealed Thin Films

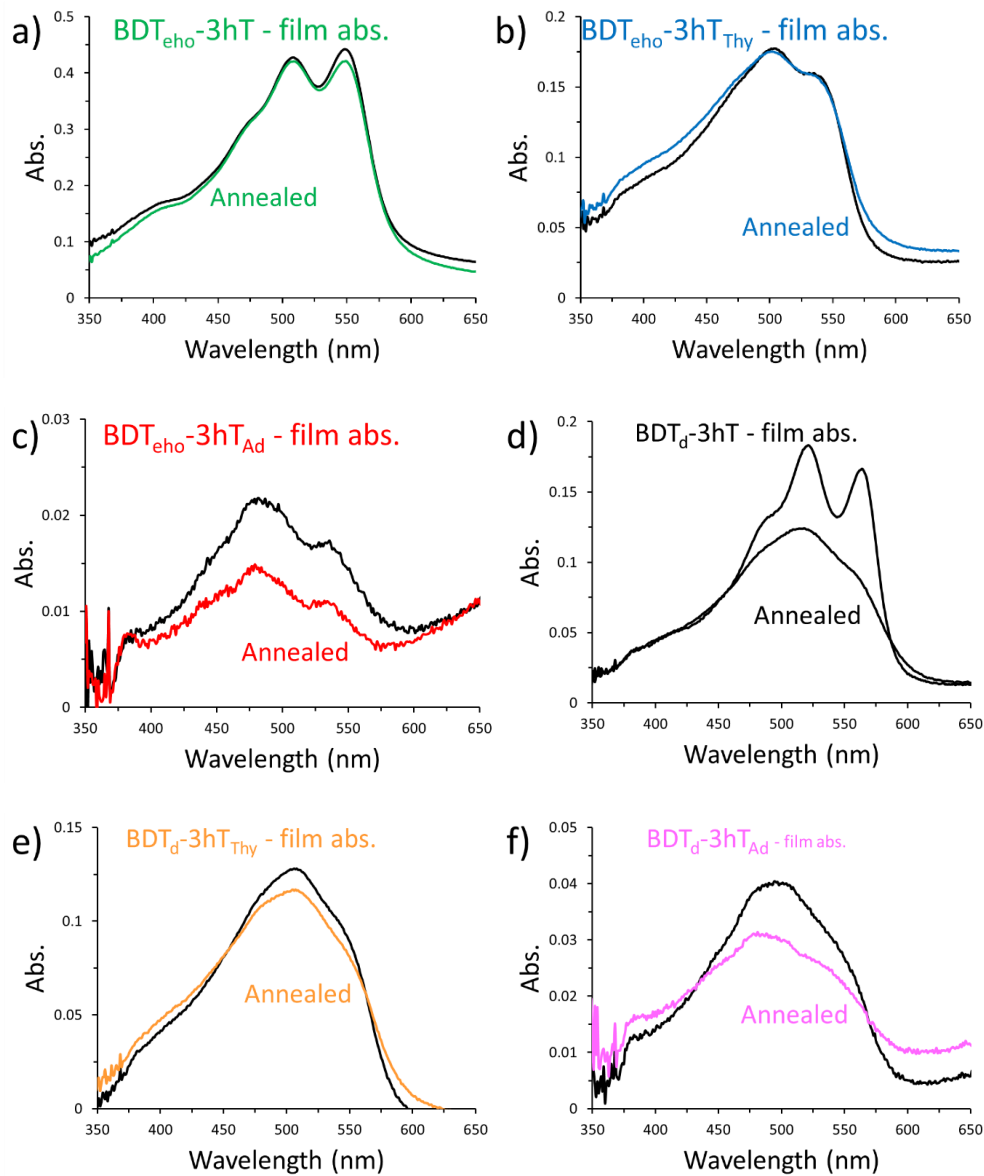


Figure S21. Absorbance spectra of films annealed at 120 °C compared to as-cast (non-annealed) thin films: a) $\text{BDT}_{\text{eho}}\text{-3hT}$, b) $\text{BDT}_{\text{eho}}\text{-3hT}_{\text{Thy}}$, c) $\text{BDT}_{\text{eho}}\text{-3hT}_{\text{Ad}}$, d) $\text{BDT}_{\text{d}}\text{-3hT}$, e) $\text{BDT}_{\text{d}}\text{-3hT}_{\text{Thy}}$, and f) $\text{BDT}_{\text{d}}\text{-3hT}_{\text{Ad}}$.

References

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