Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Chirality in DNA/π-conjugated polymer supramolecular structures: insights into self-assembly

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Characterization techniques

All NMR spectra were acquired with a Bruker Avance 300 (^{1}H 300.13 MHz, ^{13}C{^{1}H} 75.48 MHz and ^{31}P{^{1}H} 121.49 MHz) using the solvent as the chemical shift standard, except for ^{31}P{^{1}H} NMR, where the chemical shifts are relative to 85% H_3PO_4 in D_2O. All chemical shifts and coupling constants are reported in ppm and Hz, respectively. Average molecular weight and molecular weight distribution of **P3HT-Br** were measured using size exclusion chromatography (SEC) on a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL.min^{-1}), a Marathon autosampler (loop volume = 200 µL, solution conc. = 1 mg.mL^{-1}), a PL-DRI refractive index detector and three columns: a PL gel 10 µm guard column and two PL gel Mixed-B 10 µm columns (linear columns for separation of MWPS ranging from 500 to 10^6 daltons). The eluent used was THF at a flow rate of 1 mL.min^{-1} at 40°C. Polystyrene standards were used to calibrate the SEC. Matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectra were recorded using a spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J.m^{-2} delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in reflection mode at a resolution of about 10000. All samples were analyzed using *trans*-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malonitrile (DCTB). This matrix was prepared as a 20 mg.mL^{-1} solution in $CHCl_3$.[1] The matrix solution (1 µL) was applied to a stainless steel target and air dried. Polymer samples were dissolved in CH_2Cl_2 to obtain 1 mg.mL^{-1} solutions. 1 µL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 500 to 10000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time.

General procedure for the synthesis of regioregular head-to-tail poly[3-(n-bromoalkyl)thiophene-2,5-diyl] (P3HT-Br). P3HT-Br was prepared by using a Kumada Catalyst-transfer polycondensation according to literature method.[2] **P3HT-Br**: Yield: 73 %, ^{1}H NMR ($CDCl_3$): δ = 1.48 (m, 4H, CH_2), 1.73 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 2.83 (t, 2H, CH_2, $^{3}J_{H\text{-}H}$ = 6 Hz), 3.43 (t, 2H, CH_2, $^{3}J_{H\text{-}H}$ = 6 Hz), 6.98 (s, 1H, Th) ppm, UV-visible

[1] J. De Winter, G. Deshayes, F. Boon, O. Coulembier, P. Dubois, P. Gerbaux, *J. Mass Spectrom.* **2011**, *46*, 237-246.
[2] S. Clément, A. Tizit, S. Desbief, A. Mehdi, J. De Winter, P. Gerbaux, R. Lazzaroni, B. Boury, *J. Mater. Chem.* **2011**, *21*, 2733-2739.

($CHCl_3$): λ_{max} = 448 nm, SEC (THF, polystyrene standard) M_n = 13500 $g.mol^{-1}$; polydispersity = 1.27.

General procedure for the synthesis of P3HT-Im and P3HT-Py.

Poly[3-(6-bromohexyl)thiophene] (**P3HT-Br**) (1 mmol of monomer units) was allowed to react with 1-methylimidazole (8 mmol)[2] or pyridine (10 mmol) in refluxing $CHCl_3$ (20 mL) for 2 d. After cooling to room temperature, the main part of the solvent mixture was evaporated and the concentrated solution (ca. 5 mL) was poured to Et_2O to precipitate polyelectrolyte **P3HT-Im** and **P3HT-Py**. The crude polymers obtained were repeatedly washed with diethyl ether to remove residues of 1-methylimidazole or pyridine, dried under vacuum at 40°C. The solid polymers **P3HT-Im** and **P3HT-Py** were further purified with refluxing diethyl ether by using a Soxhlet apparatus and finally, dried under vacuum at 40°C.

P3HT-Im.[2] Yield : 79 %, ^{1}H NMR (CD_3OD) : δ = 1.48 (m, 4H, CH_2), 1.75 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.87 (m, 2H, CH_2), 3.97 (s, 3H, N–CH_3), 4.26 (t, 2H, CH_2, $^3J_{H\text{-}H}$ = 7 Hz), 7.15 (s, 1H, Th), 7.60 (s, 1H, $H_{ar.}$), 7.70 (s, 1H, $H_{ar.}$), 9.10 (s, 1H, NCHN) ppm. Anal. calcd.: N/S 2.00 Found 2.09.

P3HT-Py. Yield : 71 %, ^{1}H NMR (CD_3OD) : δ = 1,52 (m, 4H, CH_2), 1,74 (m, 2H, CH_2), 2,08 (m, 2H, CH_2), 2,87 (s, 2H, CH_2-Th), 4,71 (t, 2H, CH_2-N, $^3J_{H\text{-}H}$ = 6 Hz), 7,11 (s, 1H, Th), 8,12 (m, 2H, $H_{ar.}$), 8,59 (m, 1H, $H_{ar.}$), 9,10 (m, 2H, $H_{ar.}$) ppm, $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 27.6, 30.5, 30.7, 31.9, 33.0 (CH_2), 62.9 (CH_2-N), 129.9, 130.6, 132.6, 135.1, 141.8, 146.4, 147.2 ppm. Anal. calcd.: N/S 1.00 Found 0.97.

General procedure for the synthesis of P3HT-NMe_3 and P3HT-PMe_3.

Poly[3-(6-bromohexyl)thiophene] (**P3HT-Br**) (1 mmol of monomer units) was introduced into a 100 mL two necked flask equipped for stirring. 12 mL of a solution of trimethylamine[3] or trimethylphosphine (1.0 M in THF) were added and the mixture was stirred at 30°C for 24h. The observed precipitate was redissolved by adding H_2O (2 mL) and additional trimethylamine or trimethylphosphine (~3 mL) was added. The mixture was stirred at 30°C for 24 h. After removal of the solvent, the residue was dissolved in the mínimum amount of methanol and poured into Et_2O to precipitate polymers **P3HT-NMe_3** or **P3HT-PMe_3**. The crude polymers obtained were repeatedly washed with diethyl ether and dried under vacuum at 40°C. The polyelectrolytes **P3HT-NMe_3** and **P3HT-PMe_3** were further purified with refluxing diethyl ether by using a Soxhlet apparatus and finally, dried under vacuum at 40°C.

[3] J. H. Seo, A. Gutacker, Y. Sun, H. Wu, F. Hang, Y. Sao, U. Scherf, A. J. Heeger, G. C. Bazan, *J. Am. Chem. Soc.* **2011**, *133*, 8416.

P3HT-NMe$_3$. Yield : 75 %, ^{1}H NMR (CD_3OD) : δ = 1,51 (m, 4H, CH_2), 1,80 (m, 4H, CH_2), 2,87 (m, 2H, CH_2-Th), 3,15 (s, 9H, N-CH_3), 3,41 (m, 2H, CH_2-N), 7,13 (s, 1H, Th) ppm, $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 24.0, 27.2, 30.2, 30.3, 31.4 (CH_2), 53.7 (N-CH_3), 67.8 (CH_2-N), 131.7, 132.8, 136.3, 144.5 ppm. Anal. calcd.: N/S 1.00 Found 0.98.

P3HT-PMe$_3$: Yield : 77 %, ^{1}H NMR (CD_3OD) : δ = 1,38-1.80 (m, 8H, CH_2), 1,90 (m, 9H, CH_3-P), 2,29 (s, 2H, CH_2-P), 2,88 (s, 2H, CH_2-Th), 7,13 (s, 1H, Th) ppm, $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 7.38 (d, $^1J_{P\text{-}C}$ = 55 Hz), 21.5, 22.7, 23.8, 29.2, 30.5, 30.9 (CH_2), 129.0, 130.7, 133.9, 140.2 ppm, $^{31}P\{^1H\}$ RMN (CD_3OD) : δ = 27,1 (s, 1P) ppm.

Preparation of the oligonucleotides (ODN).

The buffer was prepared by using tris(hydroxymethyl)aminomethane ($(HOCH_2)_3CNH_2$), EDTA and Milli-Q water. All compounds were purchased from commercial suppliers (Aldrich) in HPLC grade. The oligonucleotides (ODN) were purchased from Eurogentec (Belgium) as HPLC-RP purification in dried format, and the purity of the ODN sequences was checked with MALDI-TOF. The oligonucleotides were dissolved in a volume of TE buffer at a concentration of 100 µM. The solution obtained was centrifuged during 2 minutes at 2000 rpm. 20 µL of this solution were used in order to prepare different aliquots. A solution of 280 µL of TE buffer was added to each aliquot in order to obtain a final volume of 300 µL and the final diluted solution was mixed using a vortex.

Preparation of the DNA – π-conjugated polymers supramolecular structures.

The concentration of the aliquot of DNA in the buffer solution was determined by UV-Vis at 25 ºC using the specific extinction coefficients (ε_{260}) of each DNA, which are 162600 L.mol^{-1}.cm^{-1}, 196100 L.mol^{-1}.cm^{-1} and 391800 L.mol^{-1}.cm^{-1} respectively for ssDNAd$(T)_{20}$, ssDNAd$(R)_{20}$ and dsDNAd$(R)_{20}$, respectively. The P3HT-Rs samples were also dissolved in TE buffer (pH 7.4, 20 mM Trisbuffer and 1 mM EDTA) and the molar ratios between polymers and DNA were adjusted using the calculated molar concentrations of DNA (around 6.67 µM). The P3HT-R solution was added to the DNA solution and both compounds were stirred using the vortex at vigorous speed during 2 minutes and allowed to equilibrate for at least 30 minutes. After that, UV-Vis and CD spectra were recorded, subtracting the corresponding baseline of the buffer solution.

UV-Vis and CD spectroscopy: The UV-Vis and circular dichroism (CD) measurements were carried out using a Chirascan^{TM} Plus CD Spectrometer from Applied Photophysics. The measurements were done using 0.1 cm quartz cells. The spectra were recorded between 210

and 650 nm, bandwidth 1 nm, time per point 1 s and 2 repetitions. As baselines, the solvent reference spectra were used and were automatically subtracted from the CD spectra of the samples. The variable temperature experiments were made using a TC 125 Temperature Controller from Quantum Northwestern simultaneously with the Chirascan™ Plus CD Spectrometer, and the temperatures were varied from 0 ºC to 80 ºC. The temperature in the quartz cells was determined using a temperature probe.

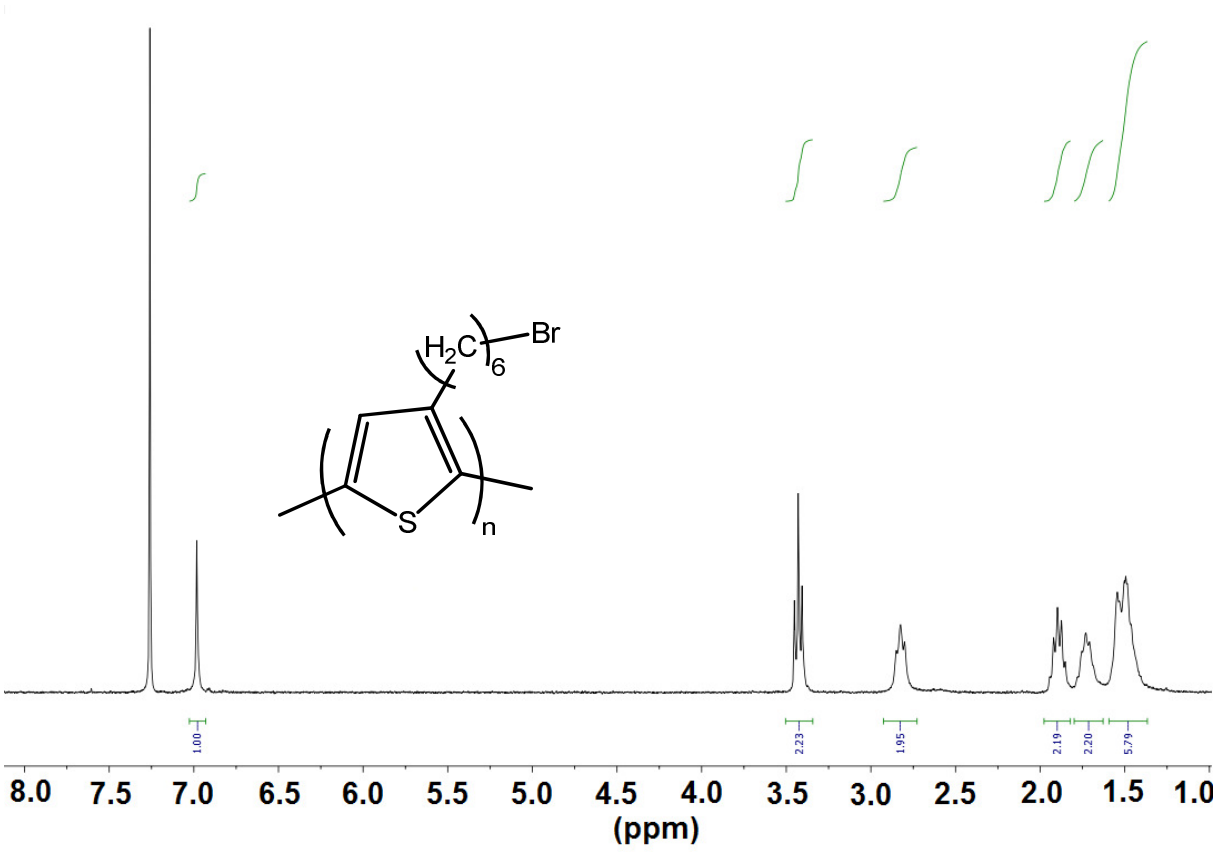

Figure S1. ^{1}H NMR spectrum of **P3HT-Br** in $CDCl_3$.

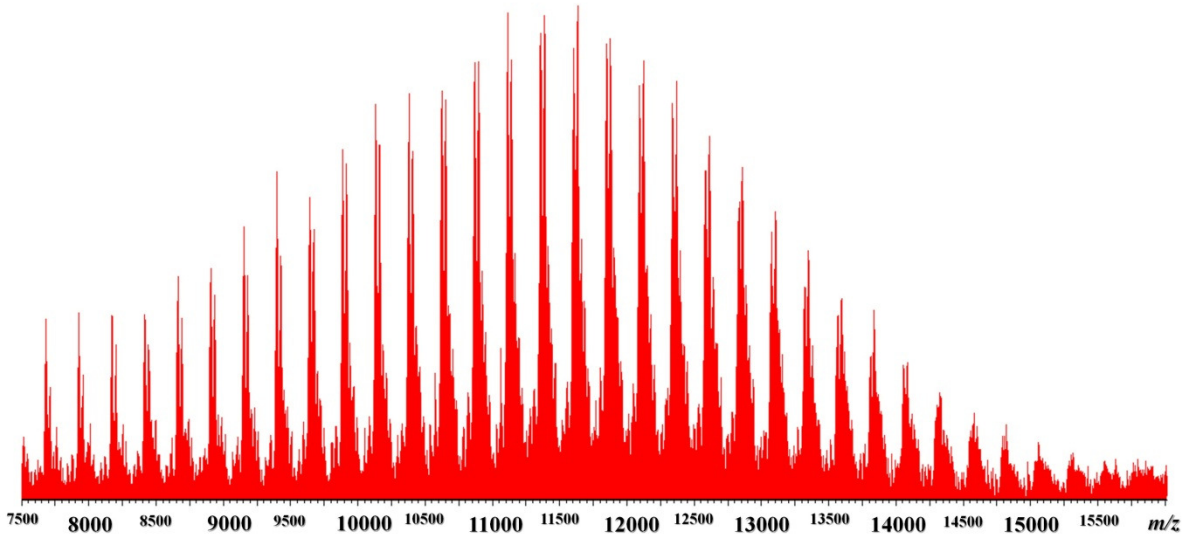

Figure S2. MALDI-TOF spectra of **P3HT-Br**.

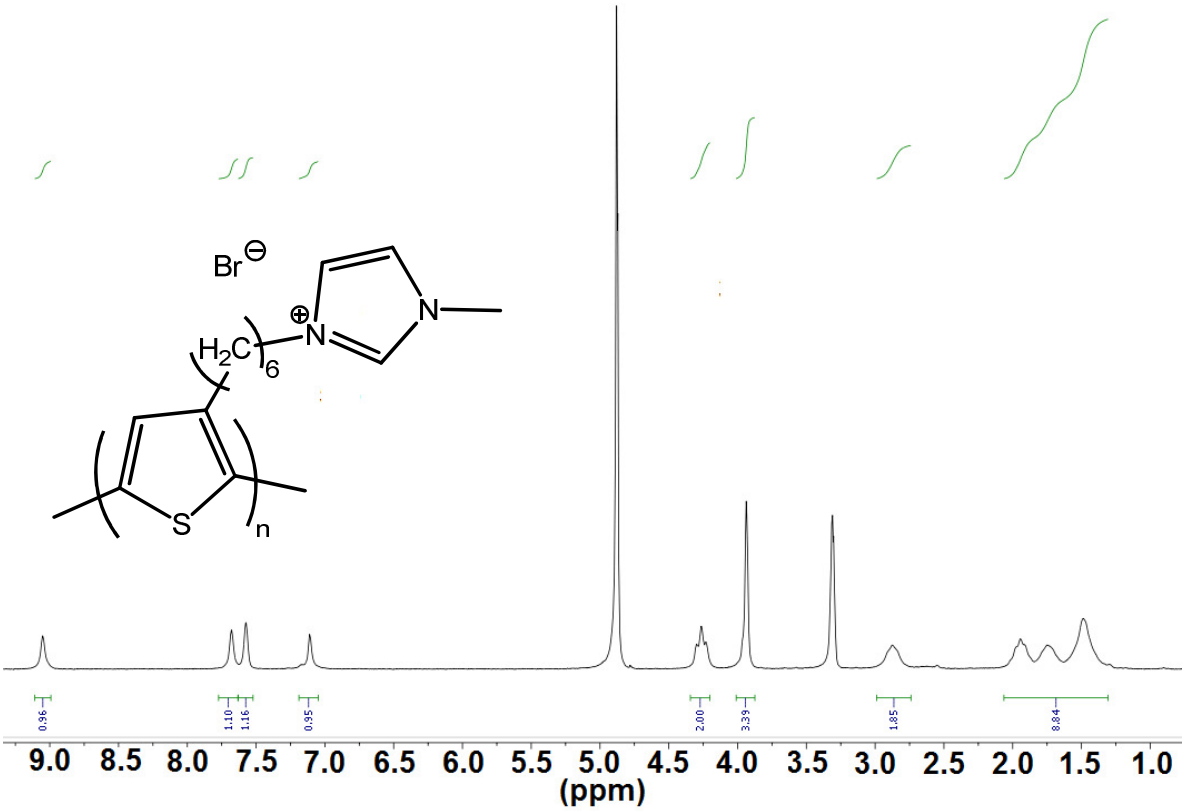

Figure S3. ^{1}H NMR spectra of **P3HT-Im** in CD_3OD.

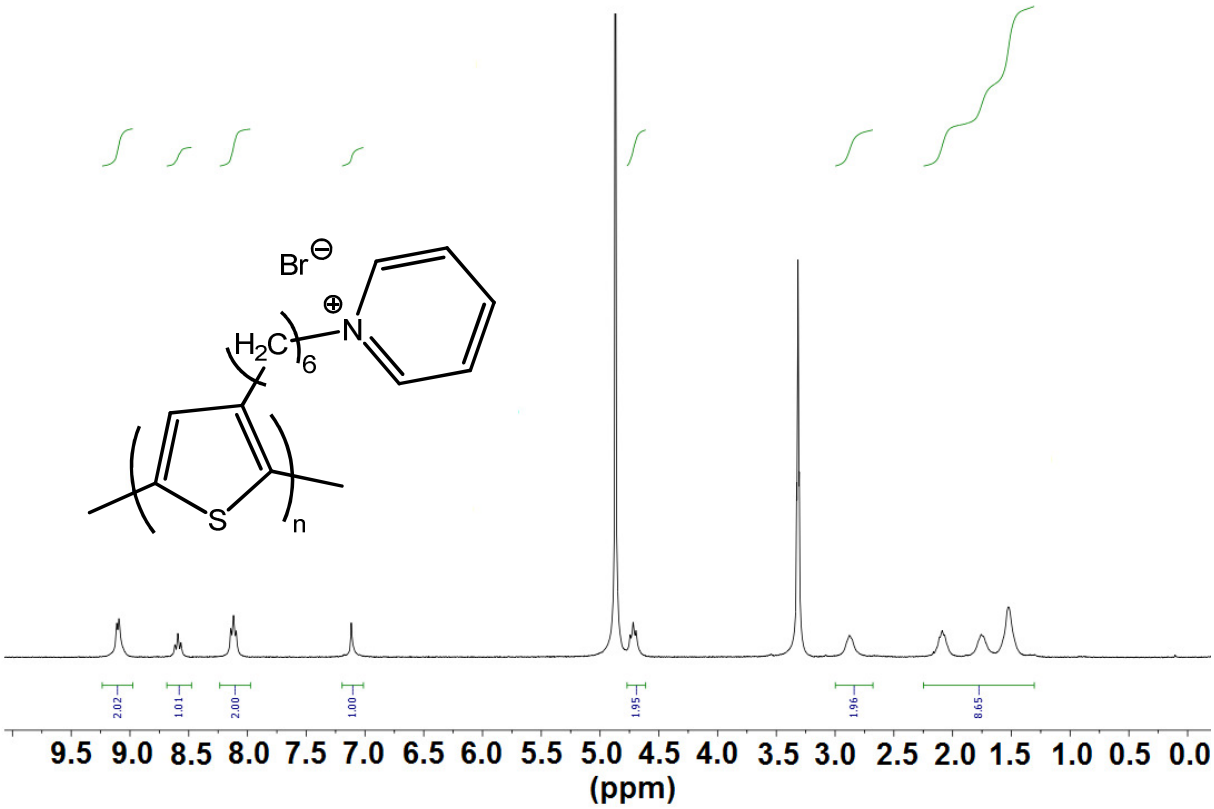

Figure S4. ^{1}H NMR spectra of **P3HT-Py** in CD_3OD.

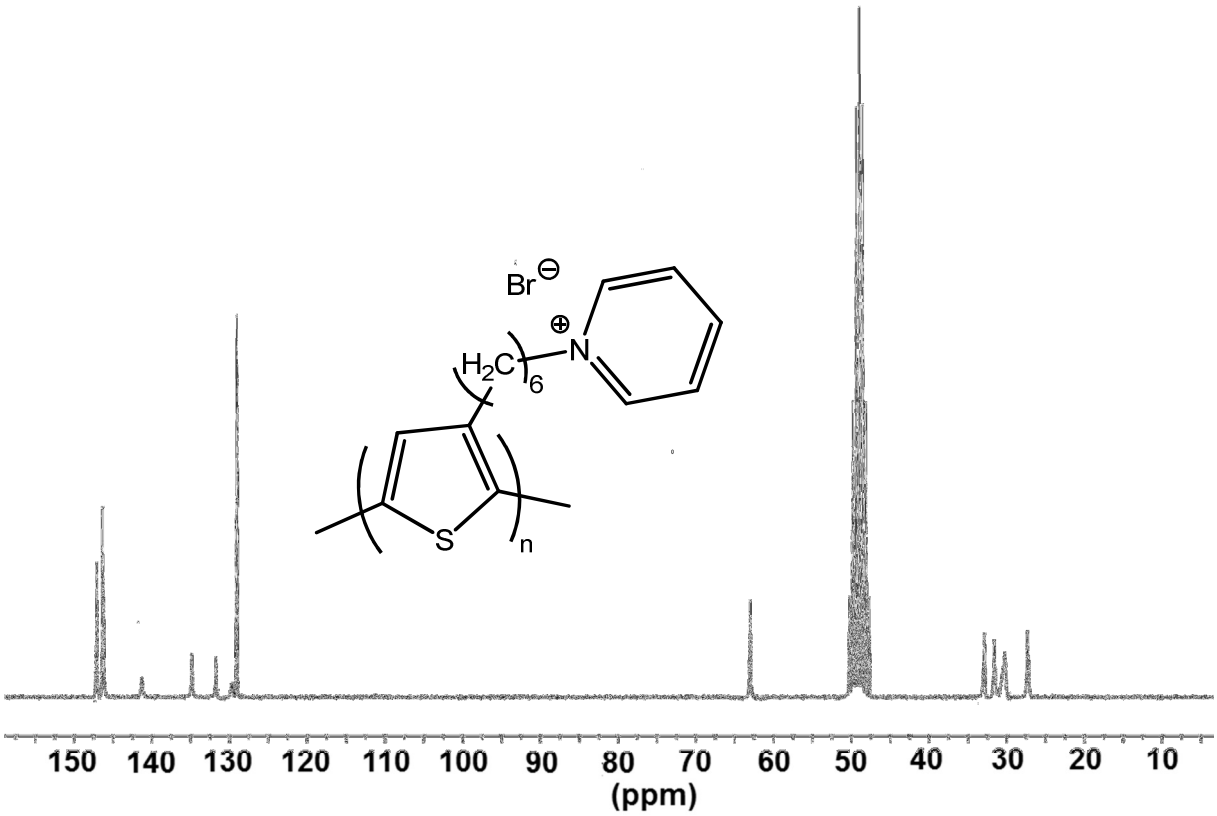

Figure S5. $^{13}C\{^{1}H\}$ NMR spectra of **P3HT-Py** in CD_3OD.

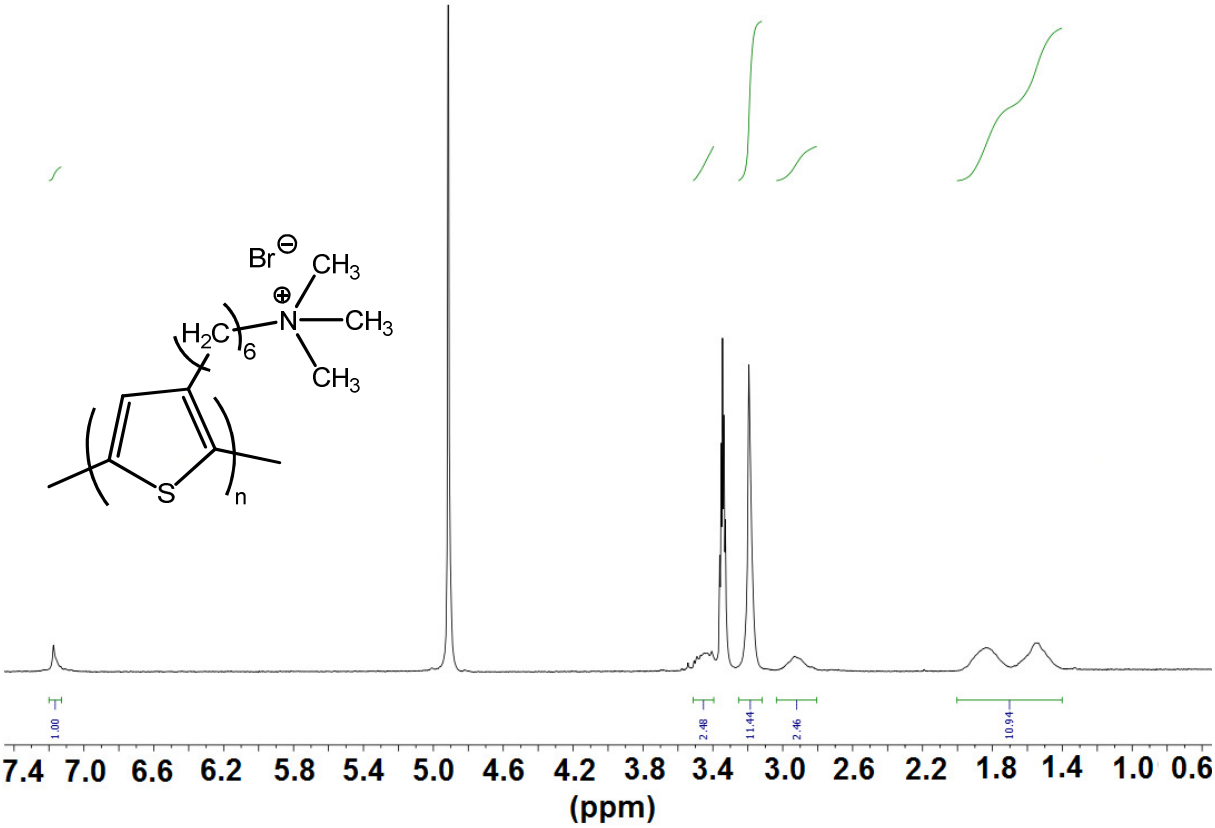

Figure S6. ^{1}H NMR spectra of **P3HT-NMe$_3$** in CD_3OD.

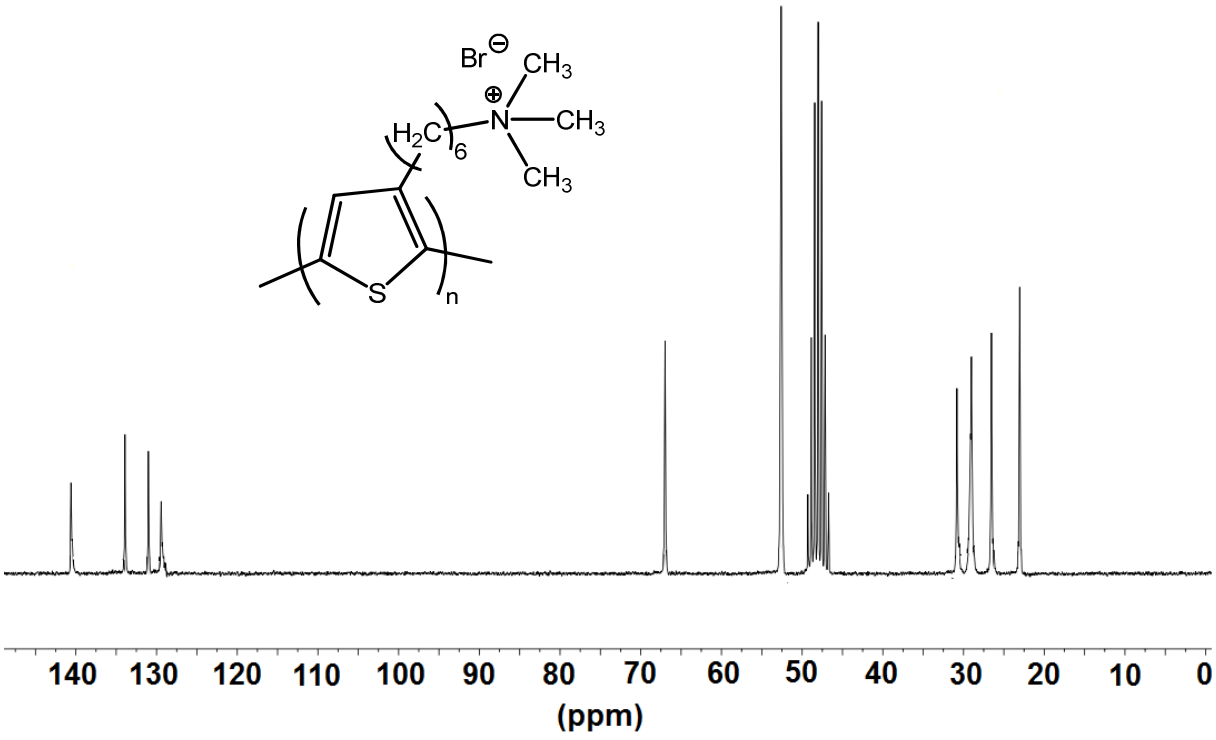

Figure S7. $^{13}C\{^{1}H\}$ NMR spectra of **P3HT-PMe$_3$** in CD_3OD.

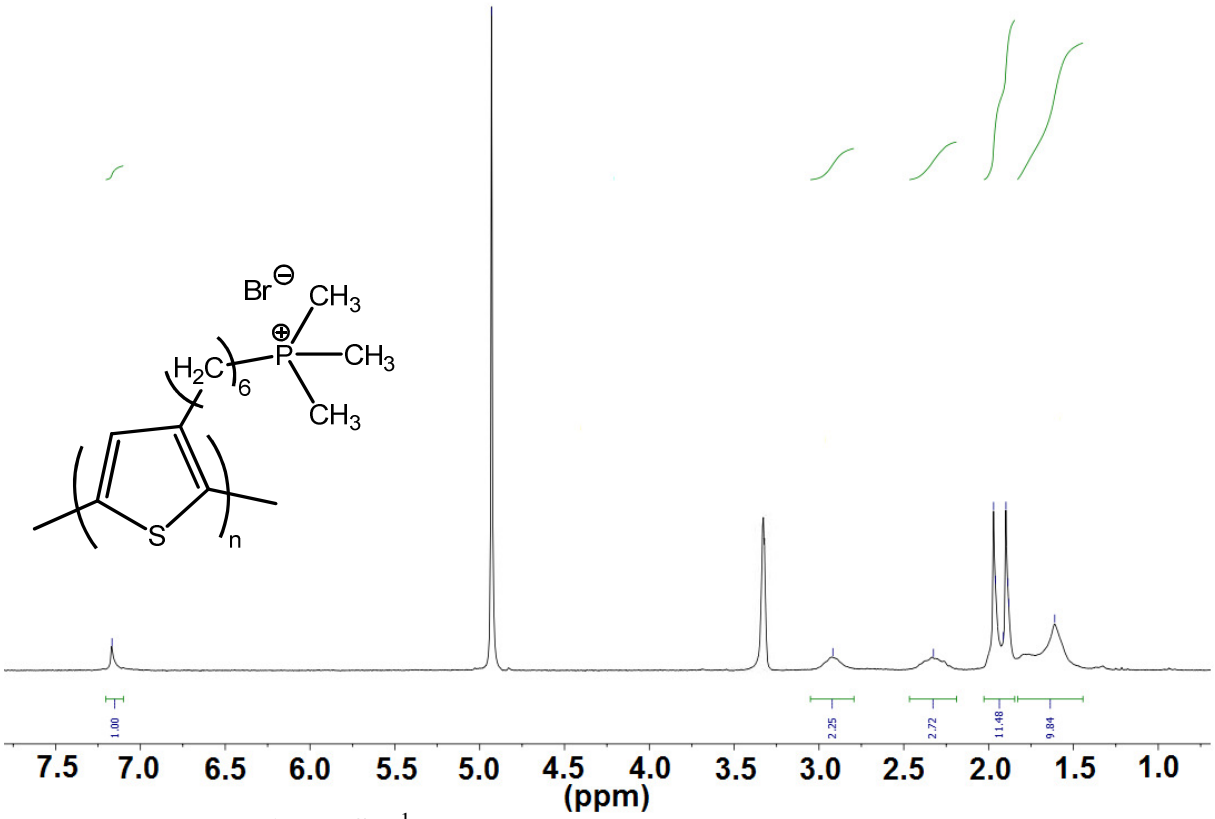

Figure S8. ^{1}H NMR spectra of **P3HT-PMe$_3$** in CD_3OD

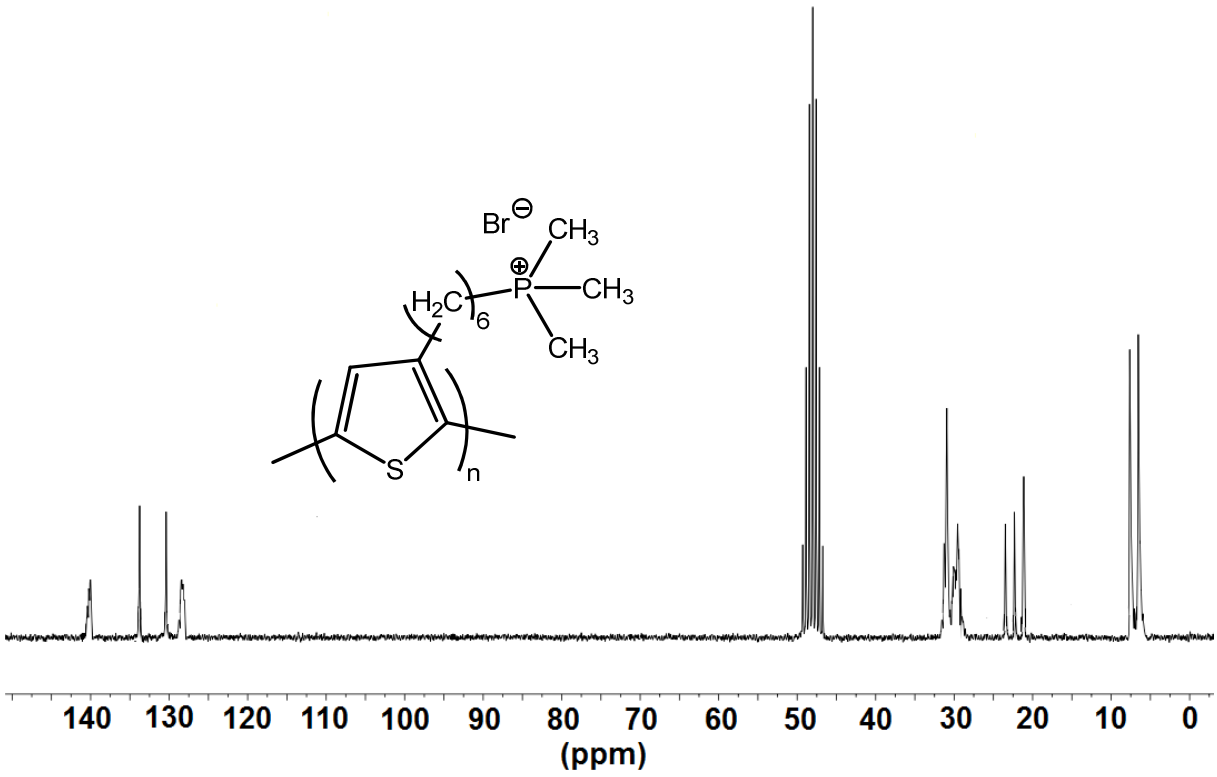

Figure S9.^{13}C{^{1}H} NMR spectra of **P3HT-PMe$_3$** in CD_3OD.

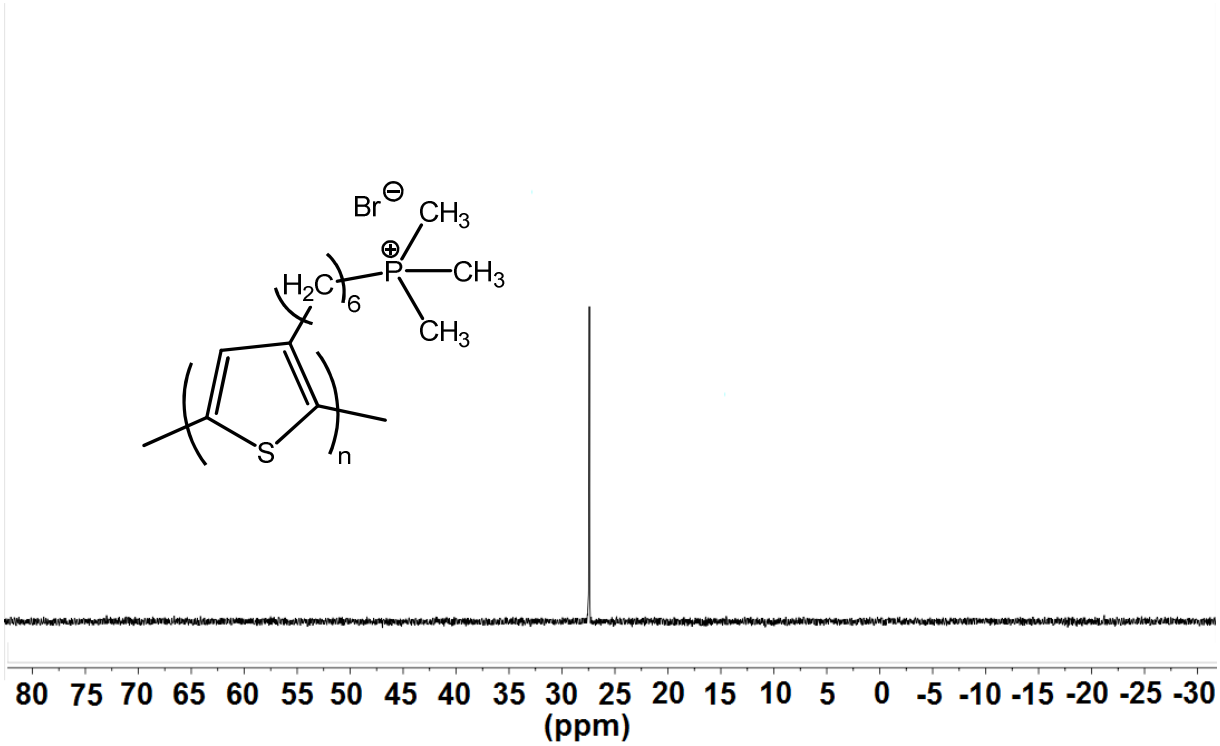

Figure S10. $^{31}P\{^{1}H\}$ NMR spectra of **P3HT-PMe$_3$** in CD_3OD.

Table S1. Absorption properties of ssDNAd(T)$_{20}$, ssDNAd(R)$_{20}$ and dsDNAd(R)$_{20}$ mixed with different **P3HT-R** polymers.

Oligonucleotide	**Polymer**[a]	Near-UV band		Vis band	
		$\lambda_{abs.max}$ (nm)	$\Delta\lambda_{abs.max}$[b]	$\lambda_{abs.max}$ (nm)	$\Delta\lambda_{abs.max}$[c]
ssDNAd(T)$_{20}$	P3HT-Im	270	+4	473	+28
ssDNAd(T)$_{20}$	P3HT-Py	260,266	-6,0	476	+12
ssDNAd(T)$_{20}$	P3HT-NMe$_3$	269	+3	473	+24
ssDNAd(T)$_{20}$	P3HT-PMe$_3$	268	+2	466	+16
ssDNAd(R)$_{20}$	P3HT-Py	260	-6	490	+26
ssDNAd(R)$_{20}$	P3HT-PMe$_3$	261	-5	486	+36
dsDNAd(R)$_{20}$	P3HT-Py	260	-6	466	+2
dsDNAd(R)$_{20}$	P3HT-PMe$_3$	262	-4	493	+43

[a]Measured at 20 °C in TE buffer (pH 7.4) at 1:1 molar ratio, ([ssDNAd(T)$_{20}$] and [xsDNAd(R)$_{20}$]) = 6.67 µM. [b]Considering $\lambda_{abs.max}$(ssDNAd(T)$_{20}$ and xsDNAd(R)$_{20}$) = 266 nm. [c]Considering $\lambda_{abs.max}$(**P3HT-Im**) = 445 nm, $\lambda_{abs.max}$(**P3HT-Py**) = 464 nm, $\lambda_{abs.max}$(**P3HT-NMe$_3$**) = 449 nm and $\lambda_{abs.max}$(**P3HT-PMe$_3$**) = 450 nm.

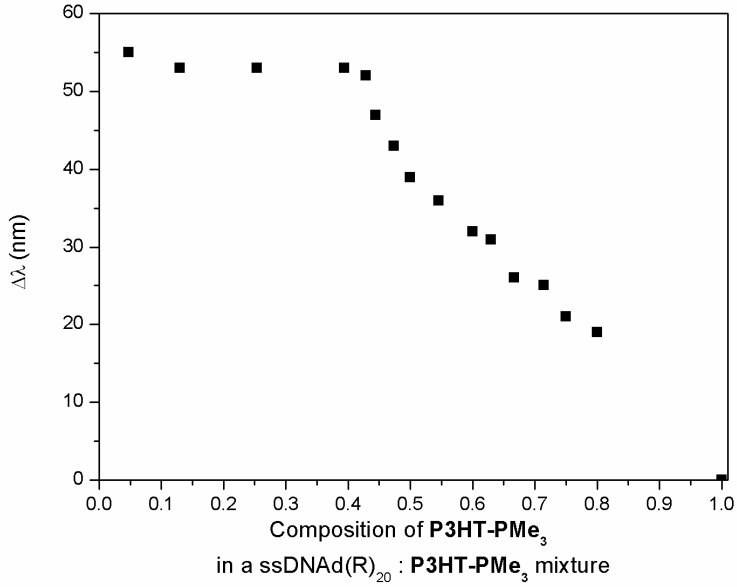

Figure S11. Shift of the absorption maximum $\Delta\lambda_{max}$ of the PT band as a function of the composition in ssDNAd(R)$_{20}$:**P3HT-PMe$_3$** mixtures.

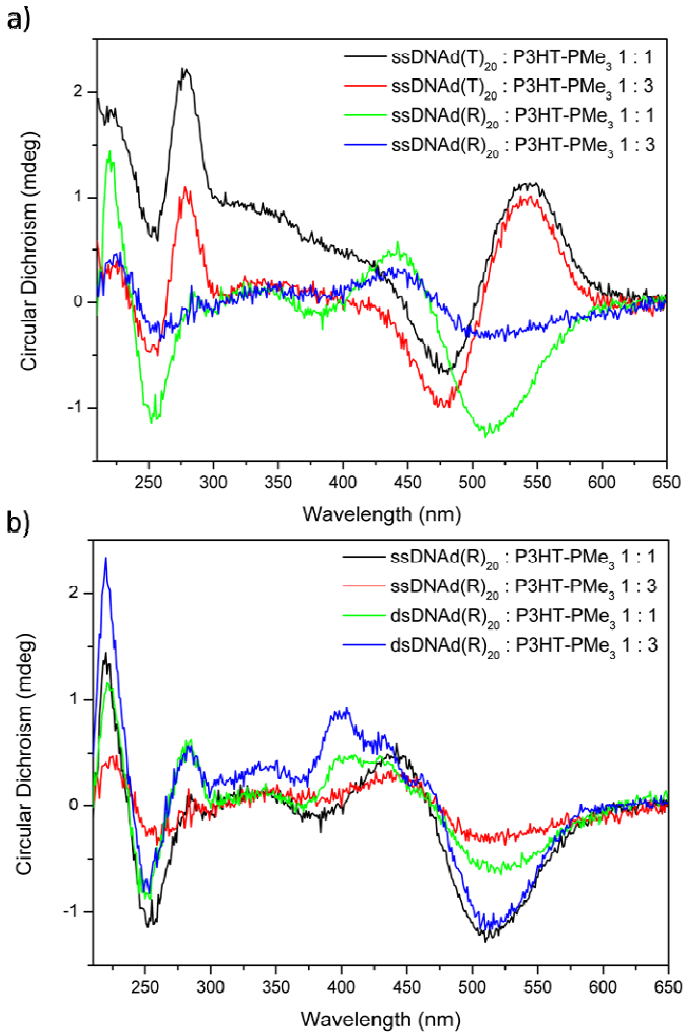

Figure S12. a) CD spectra showing the effect of the sequence, ssDNAd(T)$_{20}$:**P3HT-PMe$_3$** at 1:1 (black line) and 1:3 (red line) and CD spectra of ssDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:1 (green line) and 1:3 (blue line). b) CD spectra showing the effect of the topology: ssDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:1 (black line) and 1:3 (red line) and CD spectra of dsDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:1 (green line) and 1:3 (blue line). All the measurements were done in TE buffer, pH 7.4 at 20 ºC. [xsDNAd(X)$_{20}$] ~ 6.7 µM in all spectra.

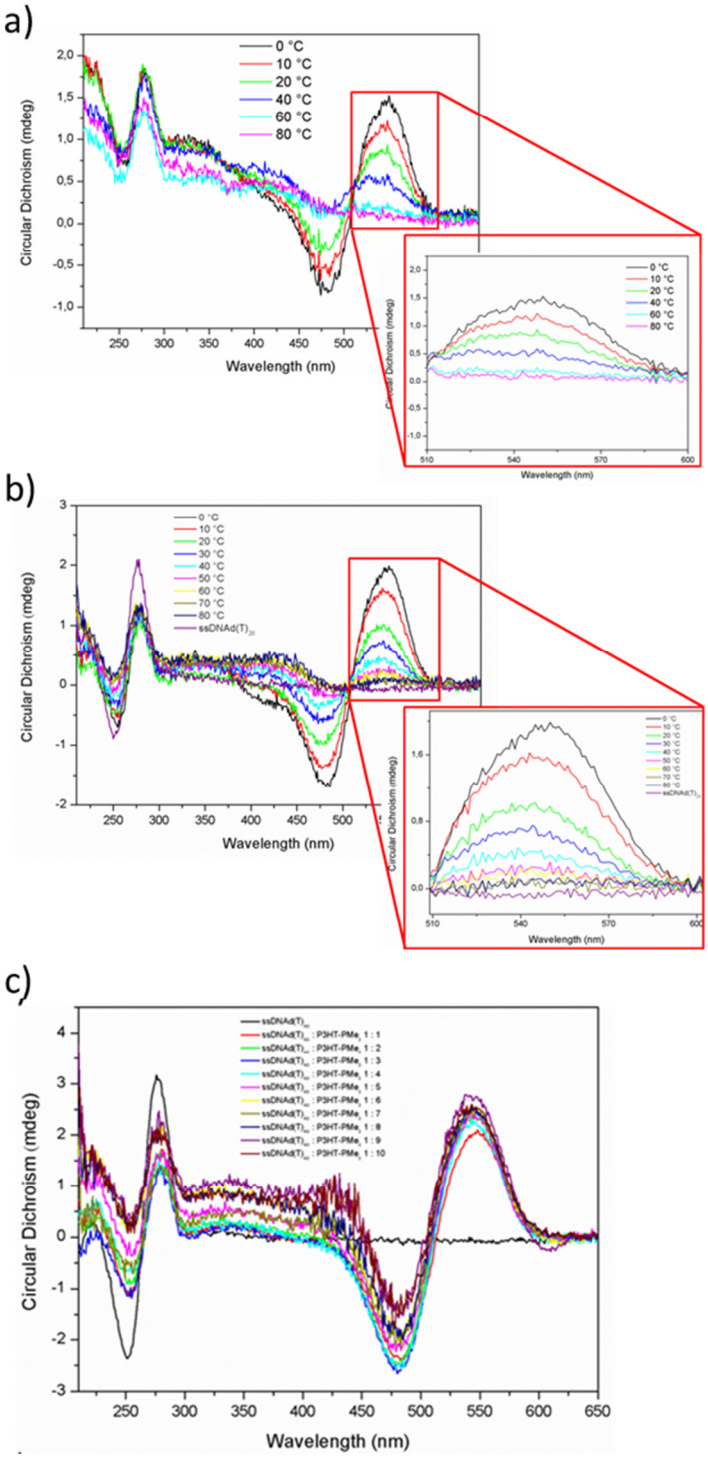

Figure S13. CD spectra of ssDNAd(T)$_{20}$:**P3HT-PMe$_3$** at a) 1 : 2 and b) 1:3 and c) 1 : N. the measurements were done in TE buffer, pH 7.4 at different temperatures for a) an b) and at 20 ºC for c). [ssDNAd(T)$_{20}$] ~ 6.7 µM in all spectra.

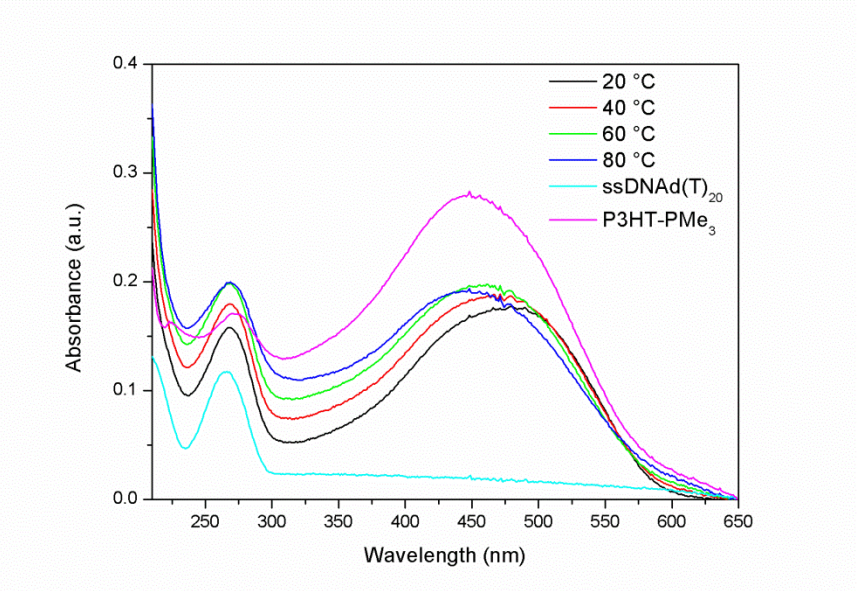

Figure S14. UV-Vis spectra of ssDNAd(T)$_{20}$:**P3HT-PMe$_3$** at 1:1. The measurements were done in TE buffer, pH 7.4 at different temperatures. [ssDNAd(T)$_{20}$] ~ 6.7 µM in all spectra.

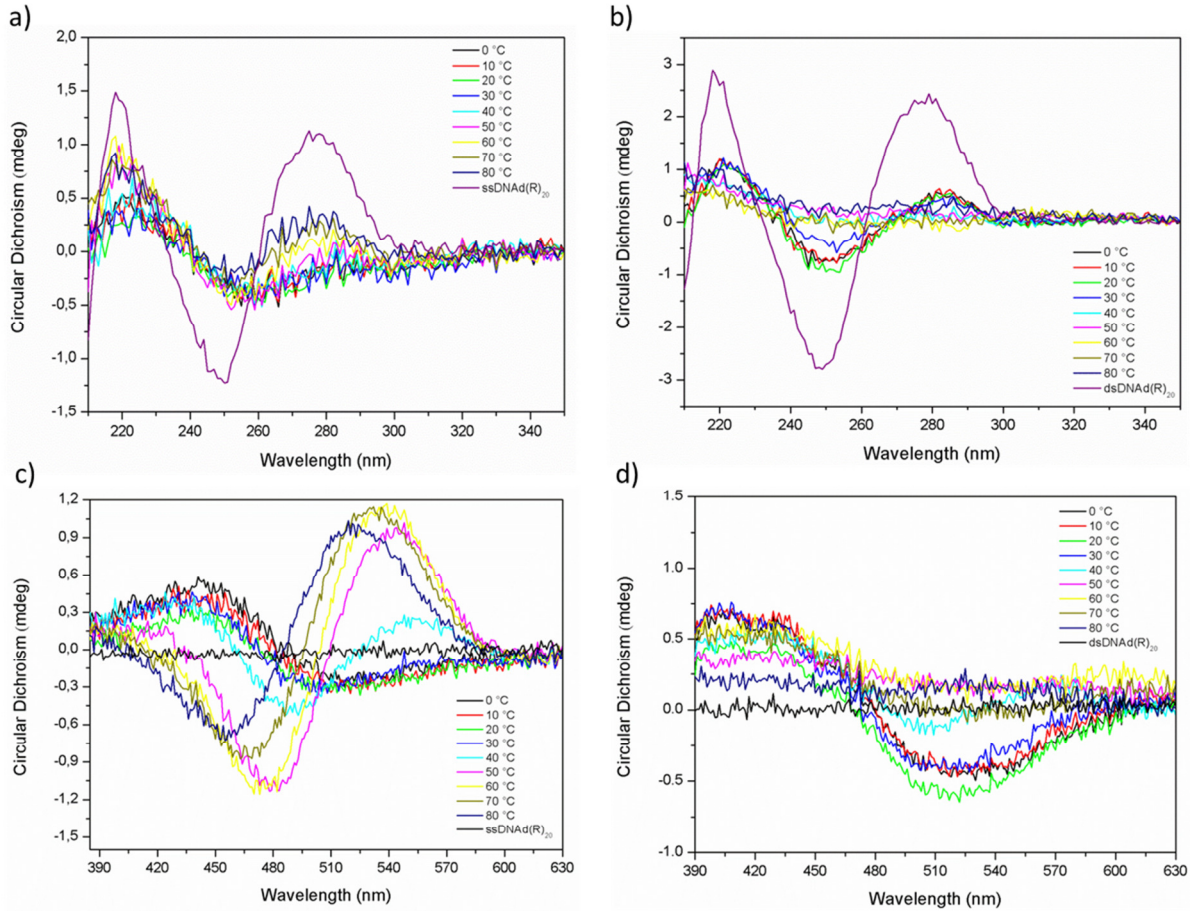

Figure S15. CD spectra of a) and c) ssDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:3 and b) and d) dsDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:1. The measurements were done in TE buffer, pH 7.4 at different temperatures. [xsDNAd(R)$_{20}$] ~ 6.7 µM in all spectra.

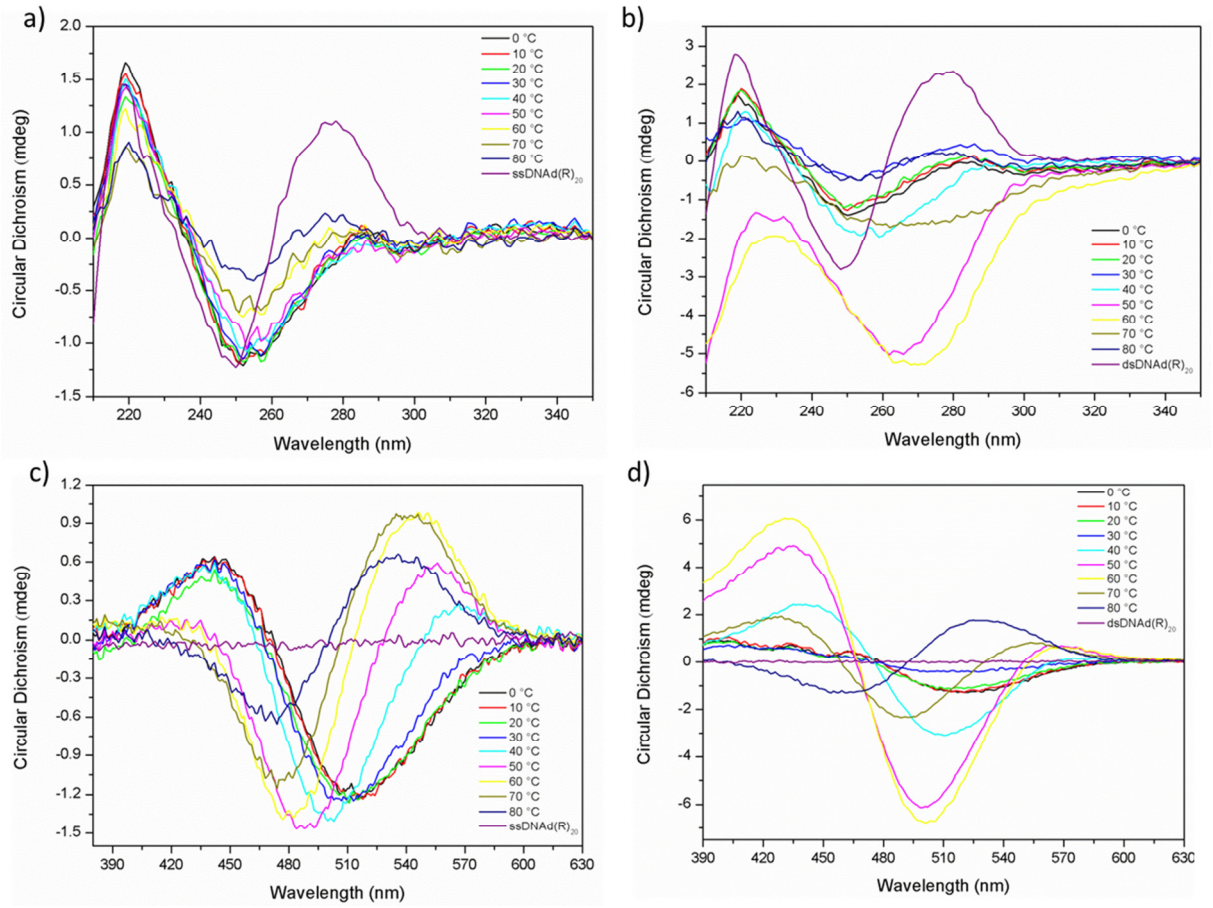

Figure S16. VT-CD spectra of a) and c) ssDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:1 ratio. b) and d): dsDNAd(R)$_{20}$:**P3HT-PMe$_3$** at 1:3 ratio. For all spectra, [xsDNAd(R)$_{20}$] ~ 6.7 μM in TE buffer, pH 7.4.

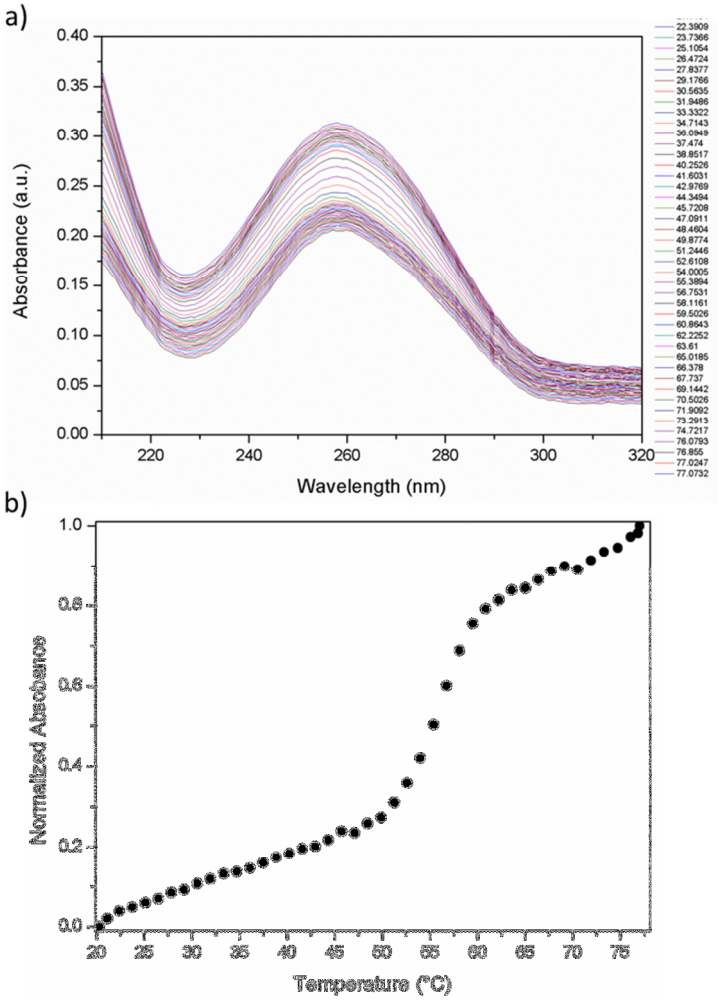

Figure S17. a) UV-Vis spectra of dsDNAd$(R)_{20}$. b) Thermal melting curves of dsDNAd$(R)_{20}$ at 260 nm. The measurements were done in TE buffer, pH 7.4 at 20 °C to 80 °C. [dsDNAd$(R)_{20}$] ~ 6.7 µM in all spectra.