Supporting Information for:

**Synthesis and Characterization of Polythiophenes with Alkenyl Substituents**

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Figure S1. $^1$H NMR spectrum of poly(3-pentenylthiophene)
Figure S2. $^1$H NMR spectrum of poly(3-undecenylthiophene)
Figure S3. $^1$H NMR spectrum of poly(3-hexylthiophene-ran-3-pentenylthiophene)
Figure S4. $^1$H NMR spectrum of poly(3-hexylthiophene-ran-3-undecenyliophene)
Figure S5. $^1$H NMR spectrum of poly{3-hexylthiophene-ran-3-(11-hydroxyundecylthiophene)}
Figure S6. Conversion vs. time plot (left) and molecular weight vs. conversion plot (right) for copolymerization of 3-hexylthiophene and 3-undecenylthiophene. Reaction conditions: [MBHT] : [MBUT] = 2 : 1; [M]₀ = 0.2 mol/L; [Ni]₀ = 0.002 mol/L.

Figure S7. TMAFM phase (left) and height (right) images of poly(3-pentenylthiophene-ran-3-hexylthiophene); scan size: 5 x 5 µm.
**Figure S8.** TMAFM phase (left) and height (right) images of poly(3-undecenylthiophene-\textit{ran}-3-hexylthiophene); scan size: 5 x 5 µm.
**Figure S9.** UV-vis spectra of poly(3-pentenylthiophene) and poly(3-undecenylthiophene) in chloroform solution.
Figure S10. UV-vis spectra of poly(3-pentenylthiophene-ran-3-hexylthiophene) and poly(3-undecenylthiophene-ran-3-hexylthiophene) in chloroform solution.
Figure S11. UV-vis spectra of poly(3-undecenylthiophene-ran-3-hexylthiophene) and poly(3-undecenylthiophene-ran-3-hexylthiophene) in thin films.
Figure S12. Cyclic voltammograms of poly(3-pentenylthiophene-ran-3-hexylthiophene) (blue) and poly(3-undecenylthiophene-ran-3-hexylthiophene) (red)

Evaluation of HOMO and LUMO energy levels was obtained by using the following equations:

\[ \text{HOMO (eV)} = -e (E_{\text{ox}} + 4.71) \text{ (eV)} \]

\[ \text{LUMO (eV)} = -e (E_{\text{red}} + 4.71) \text{ (eV)} \]

Where \( E_{\text{ox}} \) and \( E_{\text{red}} \) are the measured potentials relative to Ag/AgCl\(^+\).

Power conversion efficiency (\( \eta_p \)) was calculated from the equation shown below, where \( \eta_p \) is the ratio of maximum electrical power delivered to the incident light power (\( P_0 \)), \( J_{SC} \) is the short circuit current density, \( V_{OC} \) is the open circuit voltage and FF is the fill factor of the diode properties of the solar cell respectively.

\[ \eta_p = \frac{J_{SC} V_{OC} FF}{P_0} \]
**Figure S13.** $I$-$V$ plot of the polymer solar cell with poly(3-hexylthiophene-$\text{ran}$-3-pentylenylthiophene) donor and CdSe acceptor (weight ratio [P3] : [CdSe] = 1 : 5)

**Figure S14.** $I$-$V$ plot of the polymer solar cell with poly(3-hexylthiophene-$\text{ran}$-3-undecenythiophene) donor and CdSe acceptor (weight ratio [P4] : [CdSe] = 1 : 5)