Electronic Supplementary Information for

High-quality conjugated polymers *via* one-pot Suzuki-Miyaura homopolymerization

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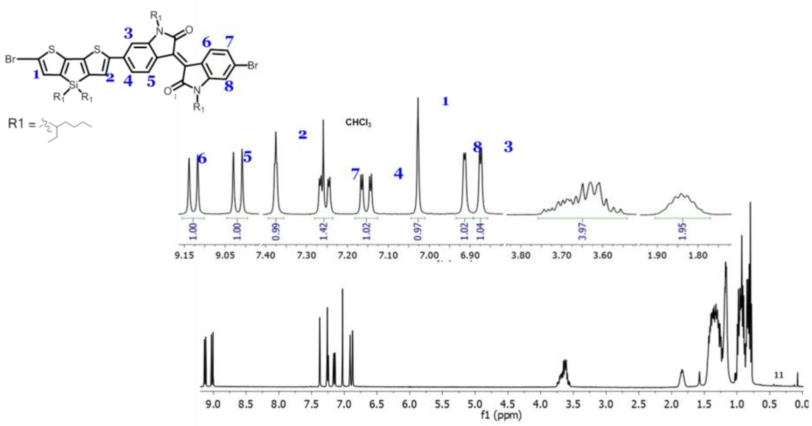
(a)



(b)

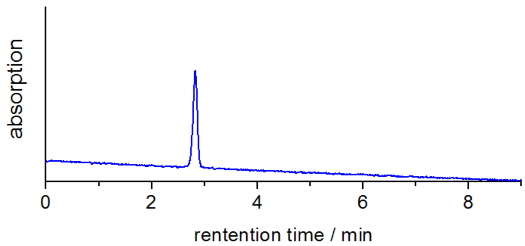


Figure S1. (a) ^{1}H NMR spectrum of the macromonomer which was used for the one-pot polymerization. Peaks of hydrogen atoms attached to aromatic carbon atoms are numbered and assigned. (b) HPLC trace @ 360 nm of the same macromonomer measured in toluene. This trace is indicative of the purity of the macromonomer.

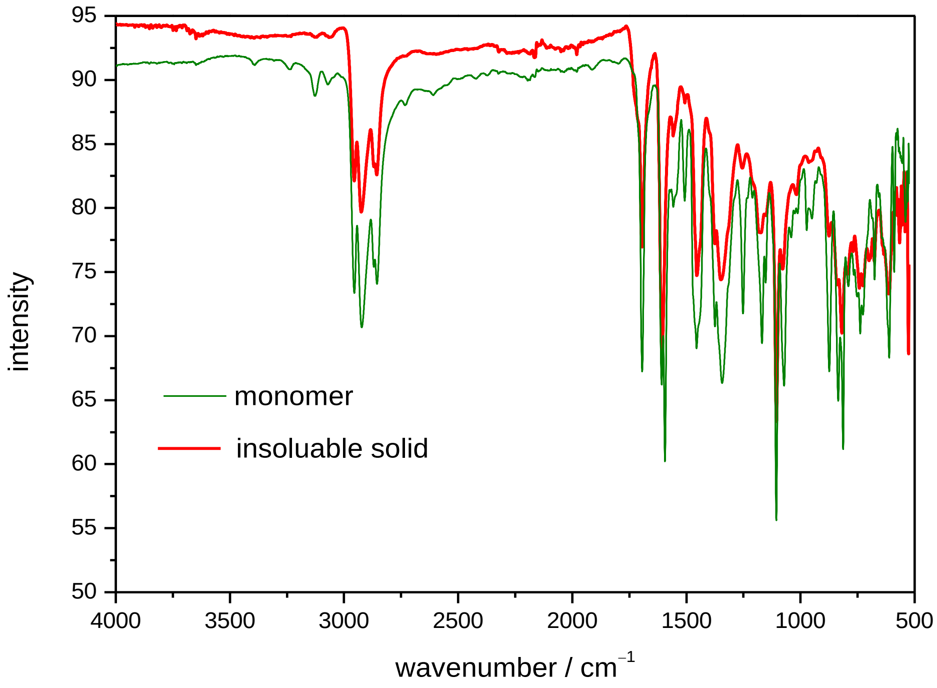


Figure S2. FT-IR spectra of the macromonomer **5** and the intractable black powder obtained from the initial polymerization attempt, as described in the manuscript. This comparison confirms the pure organic nature of the insoluble material, as well as the fact that the insoluble material is of the same chemical structure as the monomer.

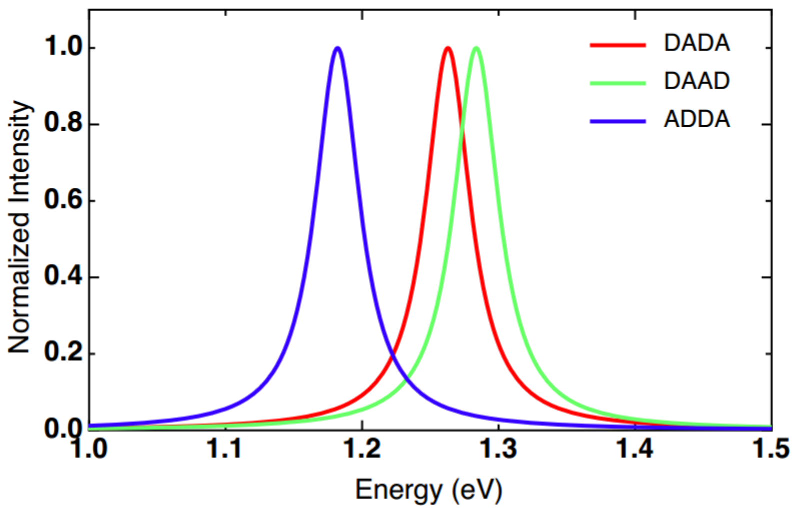


Figure S3. Calculated absorption bands of a series of dimers in the case of **P-BiPi**.

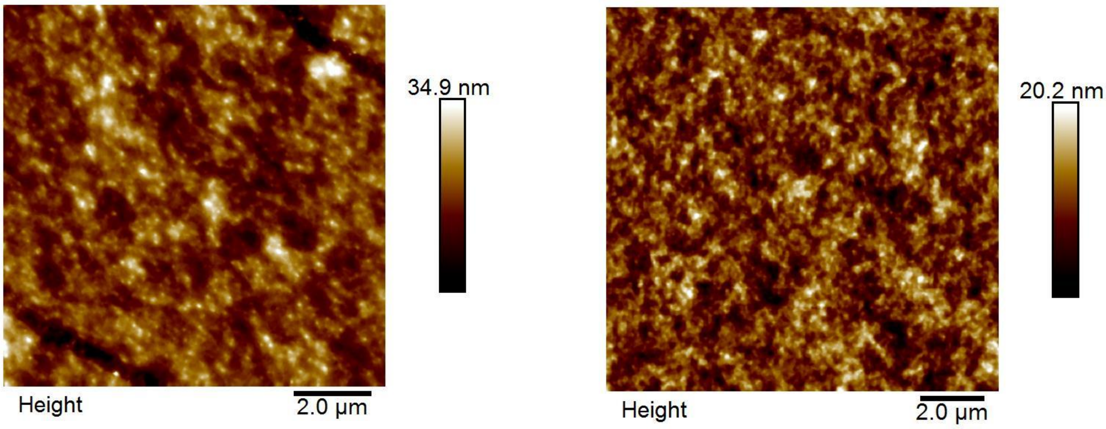


Figure S4. AFM height images of thin films of polymer:[60]PCBM blends for **P-Stille** (left) and **P-BiPi** (right).

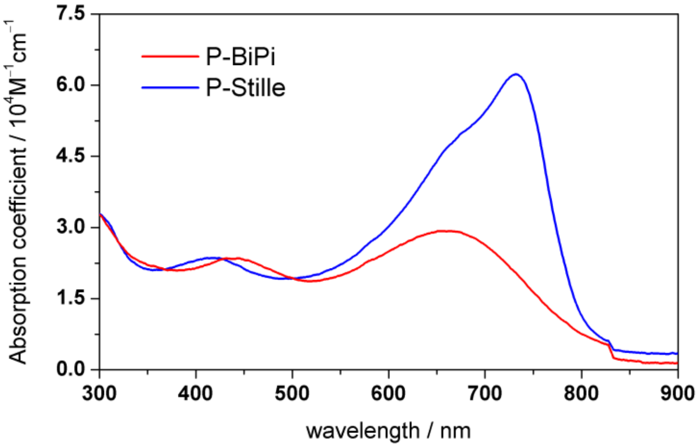


Figure S5. Comparison of the molar extinction coefficients of **P-BiPi** and **P-Stille** per repeating unit. The measurements were conducted on $CHCl_3$ solutions at 2.9 and 3.2 μg/mL for **P-BiPi** and **P-Stille**, respectively. The molar extinction coefficients per repeating unit were calculated using these mass concentrations, the molar mass of repeating units, and the measured absorbance. It is clear that **P-Stille** exhibits a much higher absorptivity from 550 nm on.

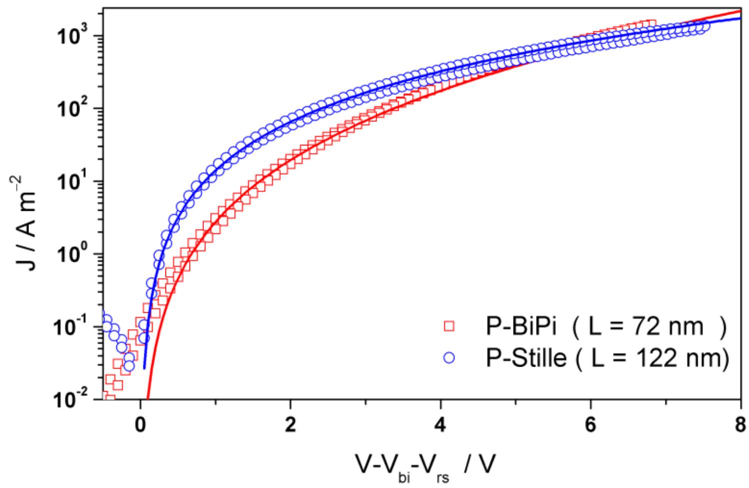


Figure S6. *J*–*V* curves of the space-charge limited current (SCLC) devices for measuring the hole mobility of **P-BiPi** and **P-Stille**. The data were fitted to modified Mott–Gurney equation:[1]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_{0n}\exp\left(0.891\gamma_n\sqrt{\frac{V_{int}}{L}}\right)\frac{V_{int}^2}{L^3}$$

where J is SCL current density, ε_e and ε_r are the electric permittivity of free space and the relative dielectric constant of the active layer respectively, μ_{0n} is the charge carrier mobility, L is the thickness of the device and γ_n is the electric field-activation factor of. The voltage on the active layer, V_{int}, is given by $V_{int}=V-V_{bi}-V_{rs}$, where V is the applied voltage, V_{bi} the built-in voltage and V_{rs} is the voltage drop due to the series resistance of the contacts.

References

1 Murgatroyd, P. N. Theory of space-charge-limited current enhanced by Frenkel effects. *J. Phys. D Appl. Phys*. **1970**, 3, 151-156.