Electronic supplementary information for

**Performance, morphology and photophysics of high open-circuit voltage, low band gap all-polymer solar cells**

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**Figure S1.** 5 μm by 5 μm AFM images of films (a) Neat BFS4, (b) neat P(NDI2OD-T2), (c) BFS4 with 1% DIO, and (d) P(NDI2OD-T2) with 1% DIO.
Figure S2. Full set of angle-resolved NEXAFS spectra of blends and neat films. The inset designates the film and interface studied, along with the average tilt angle, $<\gamma>$ of the C 1s – $\pi^*$ transition dipole moment based on the area of the $\pi^*$ manifold.
Figure S3. NEXAFS spectral fits used to determine the composition of film interfaces. For each film the spectrum taken at 55° is fit with a linear combination of neat spectra to determine the weight fraction of BFS4 at the interface. The very top graph presents neat spectra of BFS4 and P(NDI2OD-T2) for reference.
Figure S4. Composition as a function of depth of other blends determined using XPS depth profiling.
Figure S5. GIWAXS patterns of neat BFS4, (a), and P(DNI2OD-T2), (b), prepared with 1% DIO. Also shown are the GIWAXS patterns of the 3:1 BFS4:P(DNI2OD-T2) blend, (c), the 1:1 blend, (d), and the 1:2 blend.

Figure S6. Dependence the observed decay kinetics of the 2:1 blend as a function of pump fluence.
Figure S7. Intensity dependent recombination of the 2:1 blend sample. Pump fluences were 11 µJ/cm² (340 µW), 3.6 µJ/cm² (110 µW), and 1.1 µJ/cm² (35 µW).