Supporting Information

Inverted All-Polymer Solar Cells Based on a Quinoxaline-Thiophene/Naphthalene-Imide Polymer Blend Improved by Annealing

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Figure S1. Extinction coefficients of the blend film measured by ellipsometry data on the same film before annealing and after annealing. Thickness changes stays within the experiment error.



Figure S2. *J-V* curve of a) electron-only devices-ITO/PEIE/blend/LiF/Al and b) hole-only devices-ITO/PEDOT: PSS/blend/MoO₃/Al. The data was fitted by the equation $J=9/8*V^2/L^3*\epsilon*u$.



Figure S3. GIWAXS 2D pattern of neat polymer and blend films- a) as-spun blend, b) annealed blend, c) as-spun N2200, d) annealed N2200,e) as-spun TQ1, f) annealed TQ1.



Figure S4. Tapping mode topography (a-d) and phase (e-h) AFM images of pure N2200 (a, e) asspun blend (b, f), annealed blend (c, g) and pure TQ1 polymer (d, h). The scale bar is 1 μ m.



Figure S5. Tapping mode topography (a-d) and phase (e-h) AFM images of pure N2200 (a, e) asspun blend (b, f), annealed blend (c, g) and pure TQ1 polymer (d, h). The scale bar is 400 nm.



Figure S6. Scheme of the conductive-AFM setup and the energy alignment.



Figure S7. C-AFM current maps of a TQ1:N2200 blend film under forward (a) and reverse (b) bias. The bias applied to the ITO/ZnO substrate was increased from 0 to -8 V (a) or from 0 to 8 V (b) while scanning from the bottom to the top of the images, as marked by the arrows. In a) darker colors correspond to higher current values, in b) brighter colors correspond to higher current values. The two images refer to the same sample area.



Figure S8. PL quenching in the blend film. The PL quenching efficiency is estimated by:

$$\phi = 1 - \frac{PL_{blend}}{PL_{polymer}}$$

 PL_{blend} is the photoluminescence efficiency of TQ1 and N2200 in blend films. $PL_{polymer}$ is the photoluminescence efficiency of TQ1 and N2200 in neat films.



Figure S9. Electroluminescence under different applied voltages.