Supplementary Information

Phase Behaviour of Liquid-Crystalline Polymer / Fullerene Organic Photovoltaic Blends: Thermal Stability and Miscibility

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**Suppl. Fig. 1.** Refractive index $n$ (top) and extinction coefficient $k$ (bottom) of F8TBT$_{5k}$:PC$_{61}$BM thin films deduced from variable-angle spectroscopic ellipsometry (VASE) scans at 50 °C using the Standard Critical Point Model. The composition ranges from pure F8TBT$_{5k}$ to pure PC$_{61}$BM as indicated.
**Suppl. Fig. 2.** Transition temperatures of F8TBT$_{5k}$ and 20:80 F8TBT$_{5k}$:PC$_{61}$BM with respect to thin film thickness $d$. The glass transition temperatures $T_g$(F8TBT$_{5k}$) $\sim$ 104 ± 2 °C (full stars) and $T_g$(20:80 F8TBT$_{5k}$:PC$_{61}$BM) $\sim$ 98 ± 2 °C (open stars) appear independent of $d$. Whereas $T_i$(20:80 F8TBT$_{5k}$:PC$_{61}$BM) $\sim$ 138 ± 4 °C (open circles) is equally invariant, $T_i$(F8TBT$_{5k}$) $\sim$ 179 ± 2 °C (full circles) increases for $d \leq 50$ nm.

**Suppl. Fig. 3.** Absolute photoluminescence (PL) spectra of F8TBT$_{5k}$:PC$_{61}$BM binaries. Spectra were recorded under the same illumination conditions. The composition ranges from pure F8TBT$_{5k}$ to 20:80 F8TBT$_{5k}$:PC$_{61}$BM as indicated.
Suppl. Fig. 4. $J - V$ characteristics of 20:80 F8TBT$_{36k}$:PC$_{61}$BM photovoltaic devices under 1000 W m$^{-2}$ illumination. The active layer was annealed for 16 hours at the temperatures indicated before top electrode deposition (solid lines) as well as after top electrode deposition (dashed line). For completeness, dark-current characteristics are also displayed.