Supplementary Figures



Figure S1: Photographs of substrates (12 x 12 mm) showing undesirable features upon the addition of the TFB from cyclohexanone (highlighted inside dashed boxes). (a) TFB residue on an F8BT substrate annealed to just 90 °C. (b) Discontinuous TFB film formation on an F8BT substrate annealed at 155 °C for 15 minutes. (c) As in (b) but annealed for 60 minutes. Substrates (a-c) were subjected to the solvent rinse. (d) Discontinuities in TFB film on an F8BT substrate slow-cooled from the melt, though with no solvent rinse.



Figure S2: X-ray diffraction patterns of various substrates with the *d*-spacing values shown for identified peaks. Non-annealed F8BT on an ITO/ZnO substrate is observed to be amorphous (red line). The peak at 21.49 degrees is due to the ITO (211) peak as confirmed by the glass/ITO diffractogram (black line). F8BT film prepared and annealed on glass (blue line) shows a prominent peak at 5.42 corresponding to the unit cell *c*-axis spacing, as well as evidence of the b-axis (side-chain) spacing at 16.18 degrees and the π - π stacking distance at approx. 21.46 degrees. These values correspond well with those reported by Donley et al. and are evidence of the polymer backbone orienting preferentially parallel to the substrate. This orientation remains when the F8BT is annealed on an ITO/ZnO substrate (pink line), though the *c*-axis spacing peak is considerably reduced in intensity. The b-axis spacing peak is not observed and the peak at 21.5 degrees is likely to be a combination of the ITO (211) and F8BT π - π stacking distance peaks. Furthermore, two previously unreported spacings are observed and these are indicated by asterisks. ZnO therefore influences the manner in which the F8BT polymer chains pack.



Figure S3. Photos of the completed bilayer device substrates (photographed after testing). The thickness value of the TFB layer is shown under each photo. White scale bar = 5 mm.



Figure S4: xy chromaticity plots showing the changes in colour as the thickness of the polymer layer increases in (a) F8BT/TFB bilayer HyLEDs and (b) F8BT-only HyLEDs. Thickness labels correspond to total polymer layer thickness. Bilayer devices show a clear incremental change from green to orange as the device becomes thicker (indicated by the arrow), whereas such a trend is not seen in the F8BT-only devices.



Figure S5: Little change was observed between the relative intensities of the spectral features of the normalised EL with increasing forward bias in bilayer HyLEDs as shown for devices with (a) 40 nm and (b) 100 nm of TFB. The higher baseline in for the 9 V spectra in (a) is due to the noisy nature of the signal and the low level of light detected at this voltage.



Figure S6: Reflectance from the bilayer HyLED device substrates away from the MoO_3/Au contacts, i.e. through the glass/ITO/ZnO/F8BT/TFB layers. Inset: similarly for F8BT-only devices.



Figure S7: *JVL* curves of a random sample of devices for each bilayer HyLED configuration with the TFB thickness indicated above each graph.



Figure S8: Current efficiency variation with current density for the same random sample of devices presented in figure S7 for each bilayer HyLED configuration (TFB thickness indicated above each graph).