1. Differential Scanning Calorimetry

![DSC Graph](image)

**Figure S1.** First heating scan from 23 to 400°C at 10°C/min under N₂ atmosphere (50ml/min). No transitions were found in the cooling step.
2. Spectroscopic characterization of BDNA and BD3 in solution and thin film

**Figure S2.** Absorption (dotted lines) and emission (solid lines) spectra of BDNA a) in CH$_2$Cl$_2$ solution (10$^{-5}$M) (black lines) and b) in neat films (thickness 50 nm, red lines).
Figure S3. Absorption (dotted lines) and emission (solid lines) spectra of BD3 a) in CH₂Cl₂ solution (10⁻⁵M) (black lines) and b) in neat films (thickness 50 nm, red lines).
3. Morphological characterization

The morphological characterization of thin films were performed by atomic force microscopy (AFM). AFM imaging was performed on a Multimode 8 microscope equipped with a Nanoscope V controller and type J piezoelectric scanner (Bruker, USA). Samples were scanned at 0.5 Hz/line in PeakForce mode using Scanasyst-Air probes (Bruker, USA) in air, imposing an applied force of 2.5 nN. Background interpolation and quantitative surface characterization were performed with Gwyddion 2.37 (http://gwyddion.net/). SAM thicknesses and root mean squared area roughness (Sq) values were determined by averaging at least 25 μm² areas.
4. Device characteristics for BD3 and BDNA

Figure S5. (Top to bottom) Saturation transfer curves with corresponding optical power (left side) and external quantum efficiency (right side) of BD3, BDNA and DiPAXA in the same bi-layer configuration. Scales are kept the same in order to easily show the differences between the three different anthracene-based OLETs.