## Effect of dendron structures on the luminescent and charge transporting properties of solution processed OLEDs

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*Fig. S1* Thermogravimetric analysis (TGA) trace of the hosts 1, 2, and 3 with a heating rate of 10 °C min<sup>-1</sup> under nitrogen.



**Fig. S2** Heat flow traces (for the  $2^{nd}$  heating cyle) of **2** scanned from -30 °C to 240 °C with scan rates of 50 °C min<sup>-1</sup> and 100 °C min<sup>-1</sup>.



**Fig. S3** Heat flow traces (for the 2<sup>nd</sup> heating cyle) of **3** scanned from -30 °C to 240 °C with scan rates of 50 °C min<sup>-1</sup>, 100 °C min<sup>-1</sup>, and 200 °C min<sup>-1</sup>.



**Fig. S4** Cyclic voltammograms of **2** referenced to the ferrocene/ferrocenium couple measured in tetrahydrofuran (for reduction) and dichloromethane (for oxidation) at a 1 mM concentration. Measurements were conducted with a 0.1 M tetra-n-butylammonium perchlorate as the electrolyte; working electrode = glassy carbon; reference electrode = 0.01  $M AgNO_3$  in acetonitrile; counter electrode = platinum; scan rate = 100 mV s<sup>-1</sup> (for reduction) and 50 mV s<sup>-1</sup> (for oxidation).



**Fig. S5** Cyclic voltammograms of **3** referenced to the ferrocene/ferrocenium couple measured in tetrahydrofuran (for reduction) and dichloromethane (for oxidation) at a 1 mM concentration. Measurements were conducted with a 0.1 M tetra-n-butylammonium perchlorate as the electrolyte; working electrode = glassy carbon; reference electrode = 0.01  $M AgNO_3$  in acetonitrile; counter electrode = platinum; scan rate = 50 mV s<sup>-1</sup> (for reduction) and 100 mV s<sup>-1</sup> (for oxidation).



Fig. S6 Absorption coefficients of the materials.



(b)



(c)

(a)



(d)



(e)



(f)



(g)



Fig. S7 X-ray reflectometry (XRR) profiles and corresponding scattering length density (SLD) versus thickness plots (insets) for (a) TCTA, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5, (g) 6. Individual points represent experimental data and solid lines indicate the fitting curves.

Neat 1

Neat 4



11 mol% 1 & 4 blend





Neat 2

Neat 5





11 mol% 2 & 5 blend





Neat 3

Neat 6



11 mol% 3 & 6 blend



22 mol% 3 & 6 blend



Fig. S8 AFM images of the neat and blend films.



*Fig. S9 Grazing incidence X-ray diffraction spectra of compounds. Data has been offset for clarity and the 3:6 blends are in mol%.*