

# Silicon phthalocyanines as dopant emitters for efficient solution processed OLEDs

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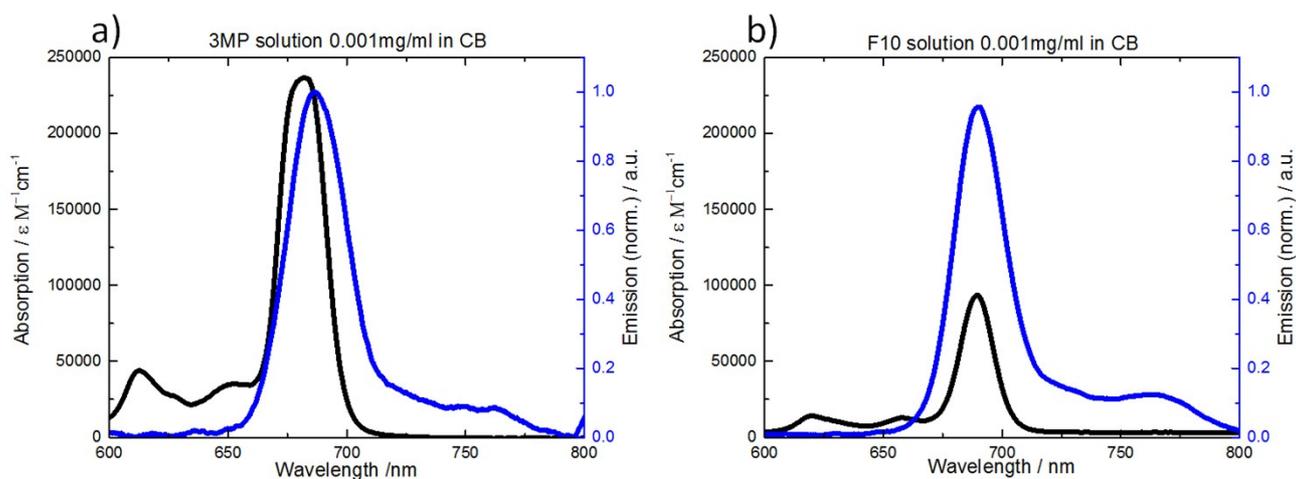
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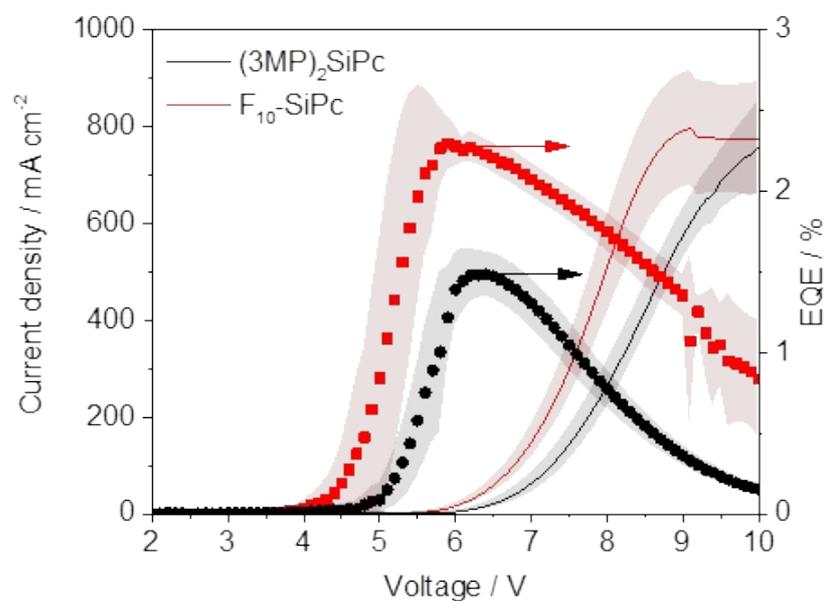
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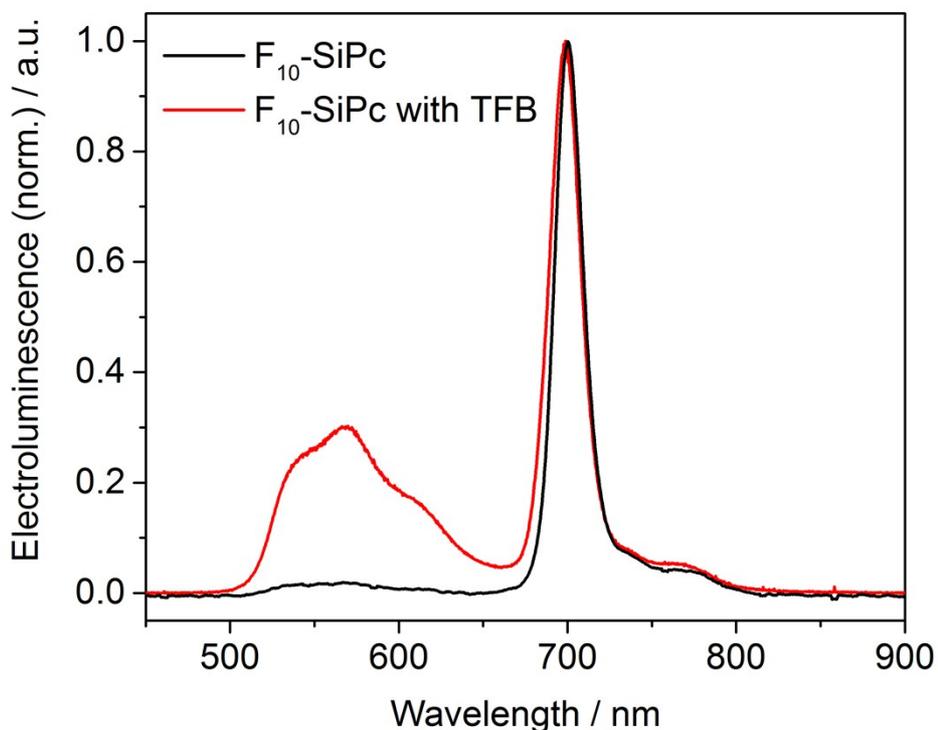
## Electronic Supporting Information



**Figure S1:** Weighted absorption and emission for a) (3MP)<sub>2</sub>-SiPc and b) F<sub>10</sub>-SiPc. Compared with the normalised emission, this data provides a measure of the relative degree of self-absorption between the two dopants. Integration of the spectral overlap region indicates that (3MP)<sub>2</sub>-SiPc is 2.9 times more prone to self-absorption than F<sub>10</sub>-SiPc at the same weight concentration in dilute solution, which likely explains the reduced solution PLQE.

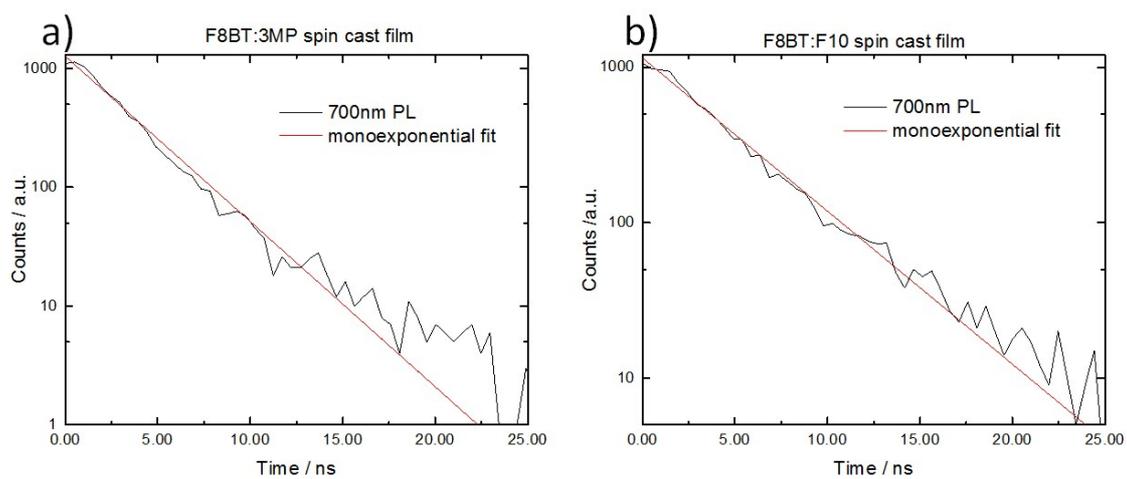


**Figure S2:** Current density-voltage (lines) and EQE-voltage (symbols) characteristics for the optimised OLED devices. Shaded regions correspond to one standard deviation in device-to-device variability. Six devices were tested for each dopant.

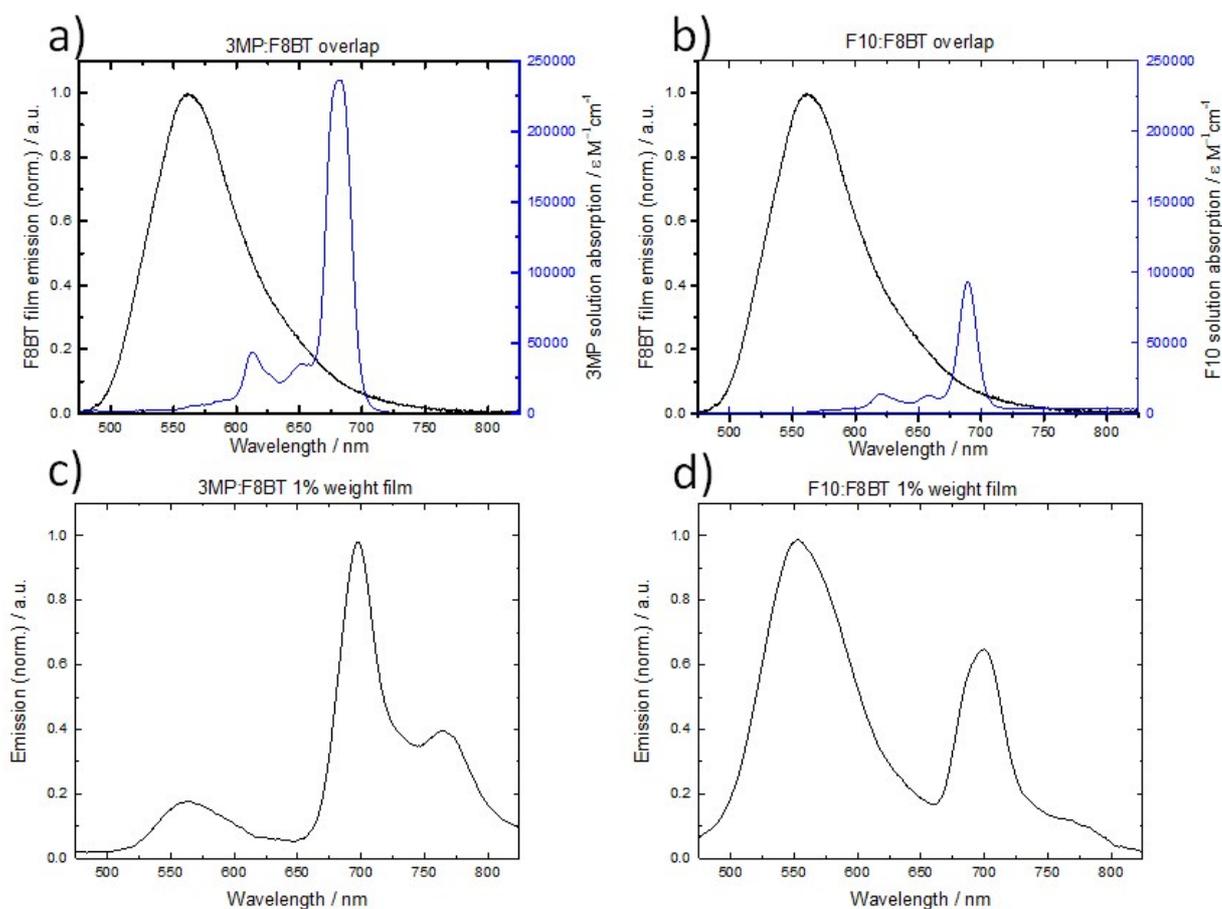


**Figure S3.** Electroluminescence of OLED device with TFB hole-injection layer relative to based device.

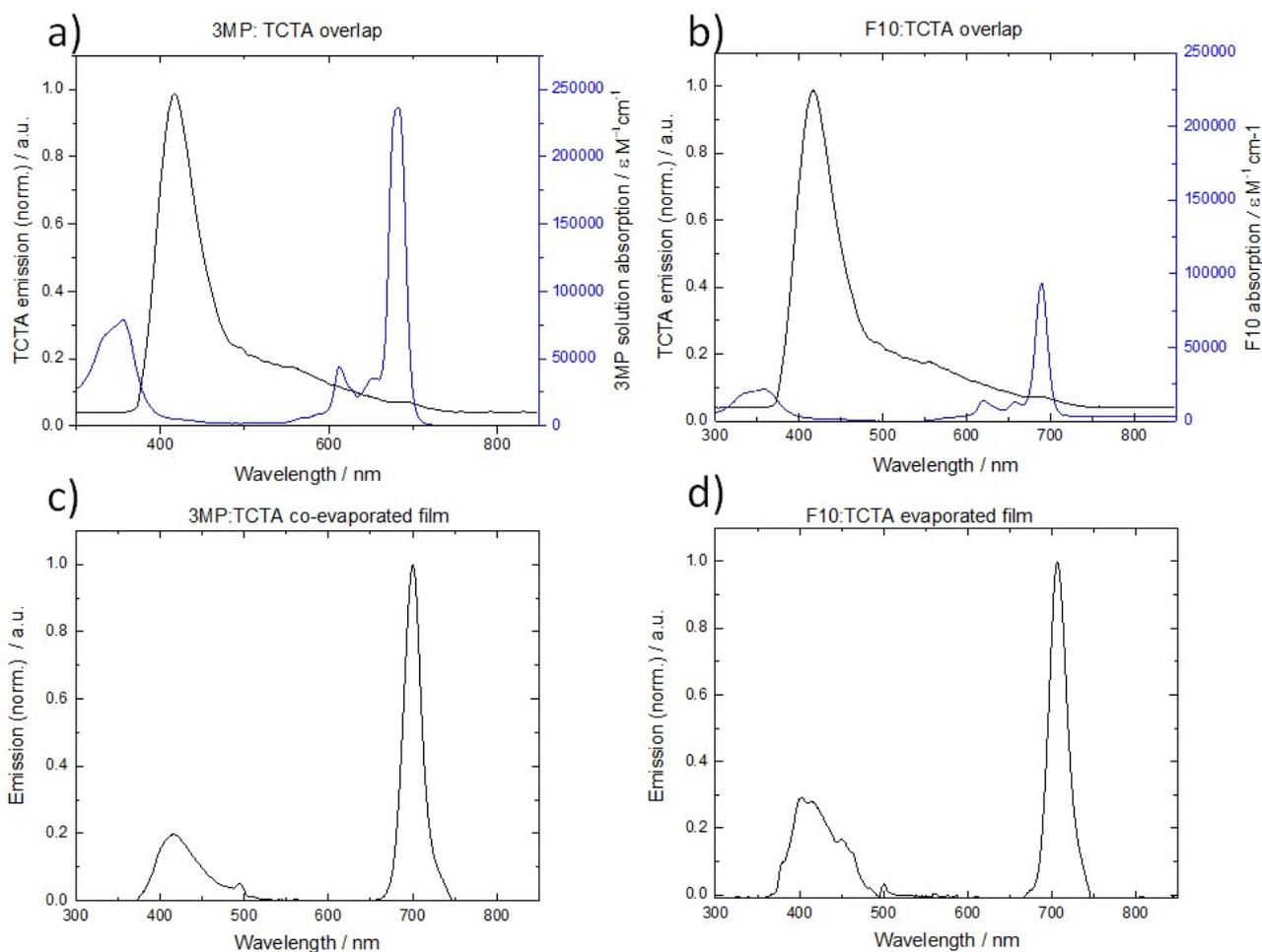
**Comment:** During device optimization of our solution-processed  $F_{10}$ -SiPc OLEDs we trialed the inclusion of a thin TFB layer as a means to optimize hole injection. Whilst these devices worked with reasonable efficiency (peak EQEs of  $\sim 2\%$ ) their electroluminescence contained a greater proportion of residual F8BT host emission (data presented in Figure 1). Because this feature reduces the colour purity of the OLEDs we concluded that the presence of TFB in the OLED stack was not a promising step forward at this stage of our research. Extensive development of the device - including steps to increase the active layer guest concentration without inducing emission quenching - could result in further improvements in performance and we feel that such work is best-suited for a follow-up investigation.



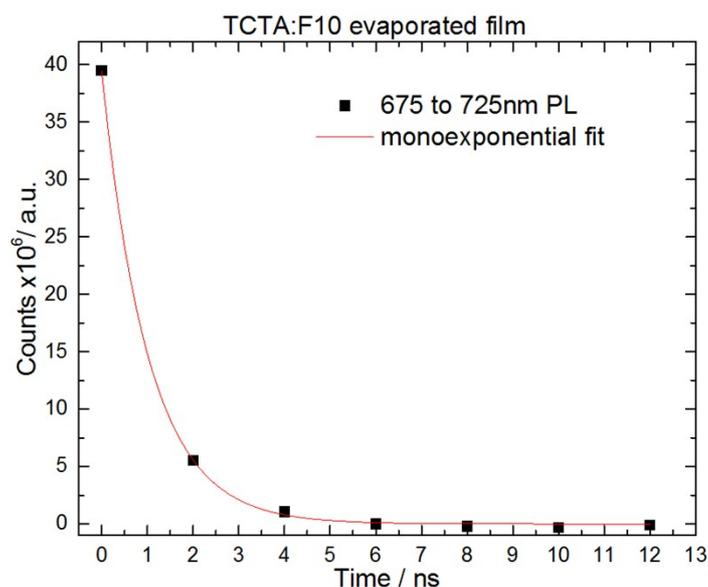
**Figure S4:** PL decay lifetimes for a) F8BT:(3MP)<sub>2</sub>-SiPc and b) F8BT:F<sub>10</sub>-SiPc blend thin films, prepared in an identical manner to the films used for optimised OLEDs.



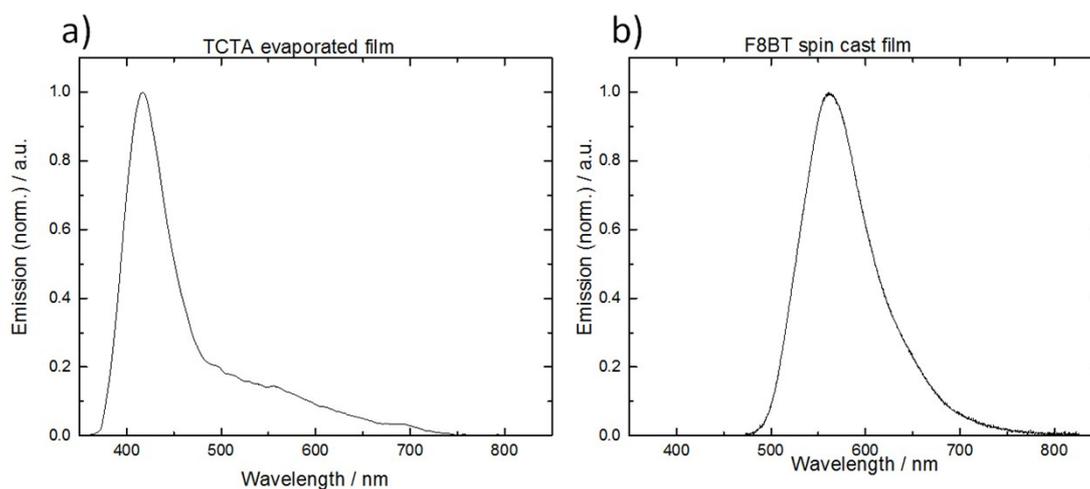
**Figure S5:** a) and b) show the overlap of the F8BT emission with the weighted  $(3MP)_2$ -SiPc and  $F_{10}$ -SiPc absorption respectively. The relative strength of the transfer overlap is in good agreement with the degree of quenching of host emission seen in the photo-excited blend films (parts c) and d), also presented in the main text). The transfer overlap of  $(3MP)_2$ -SiPc is 3.6 times larger than for the  $F_{10}$ -SiPc, and in the blend films there is 2.6 times more PL from the  $(3MP)_2$ -SiPc as a fraction of the total emission.



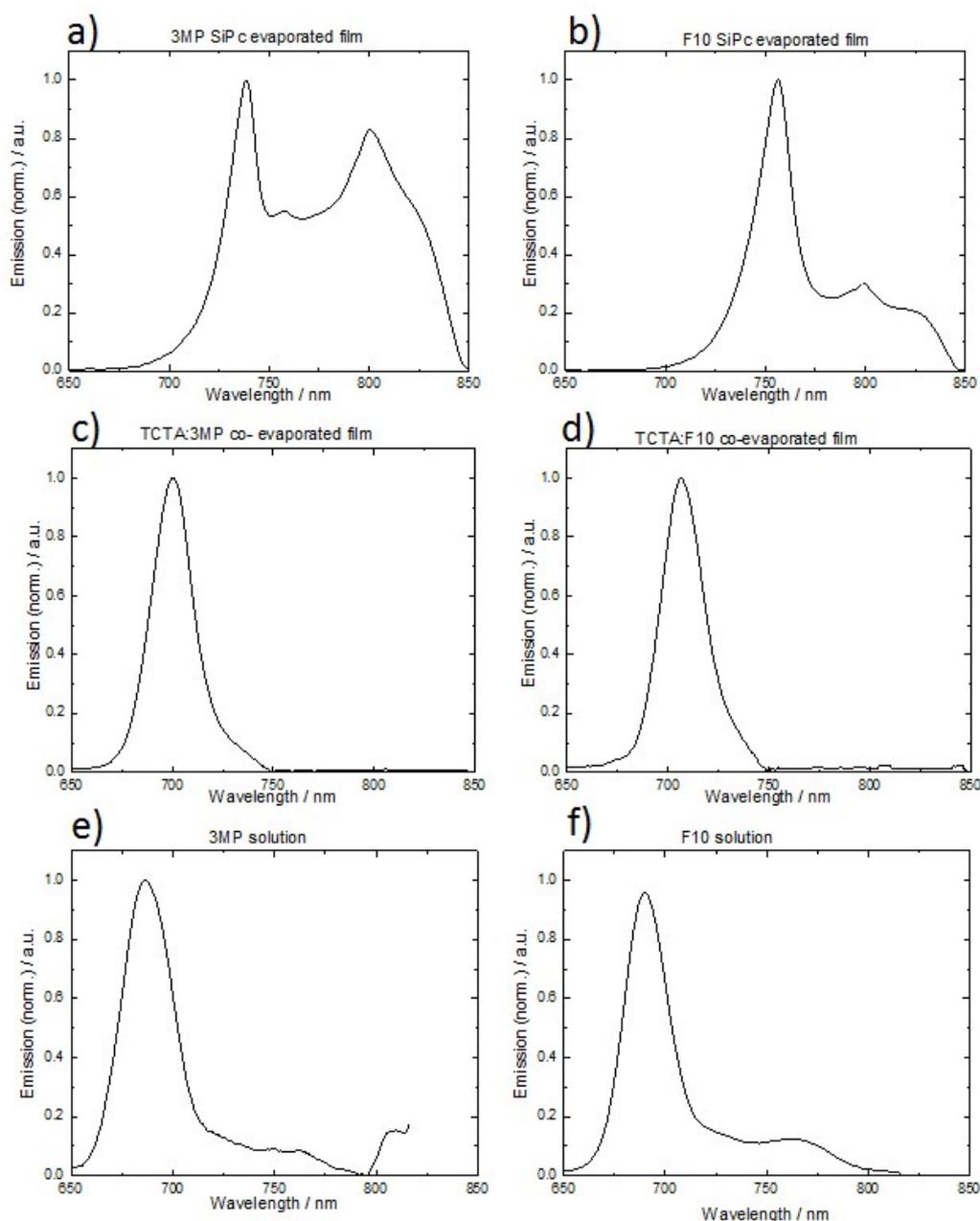
**Figure S6:** a) and b) overlap of the TCTA emission with the weighted (3MP)<sub>2</sub>-SiPc and F<sub>10</sub>-SiPc dilute solution absorption respectively. The use of the 375nm long pass in the measurement of the TCTA PL means that this is likely an underestimate of the energy transfer from this host, as there would be more overlap with the SiPc UV absorption band. In parts c) and d) some degree of quenching in the host PL is evidenced in the blend films, demonstrating energy transfer from the TCTA to (3MP)<sub>2</sub>-SiPc and F<sub>10</sub>-SiPc co-evaporated at 5% weight.



**Figure S7:** PL spectrum and decay lifetime for a TCTA:F<sub>10</sub>-SiPc (95:5 wt), prepared in an identical manner to the film used for vacuum-processed OLEDs. The shorter lifetime found here is due in part to the higher fluence of the 360 nm excitation versus the 405 nm excitation used for all other measurements.

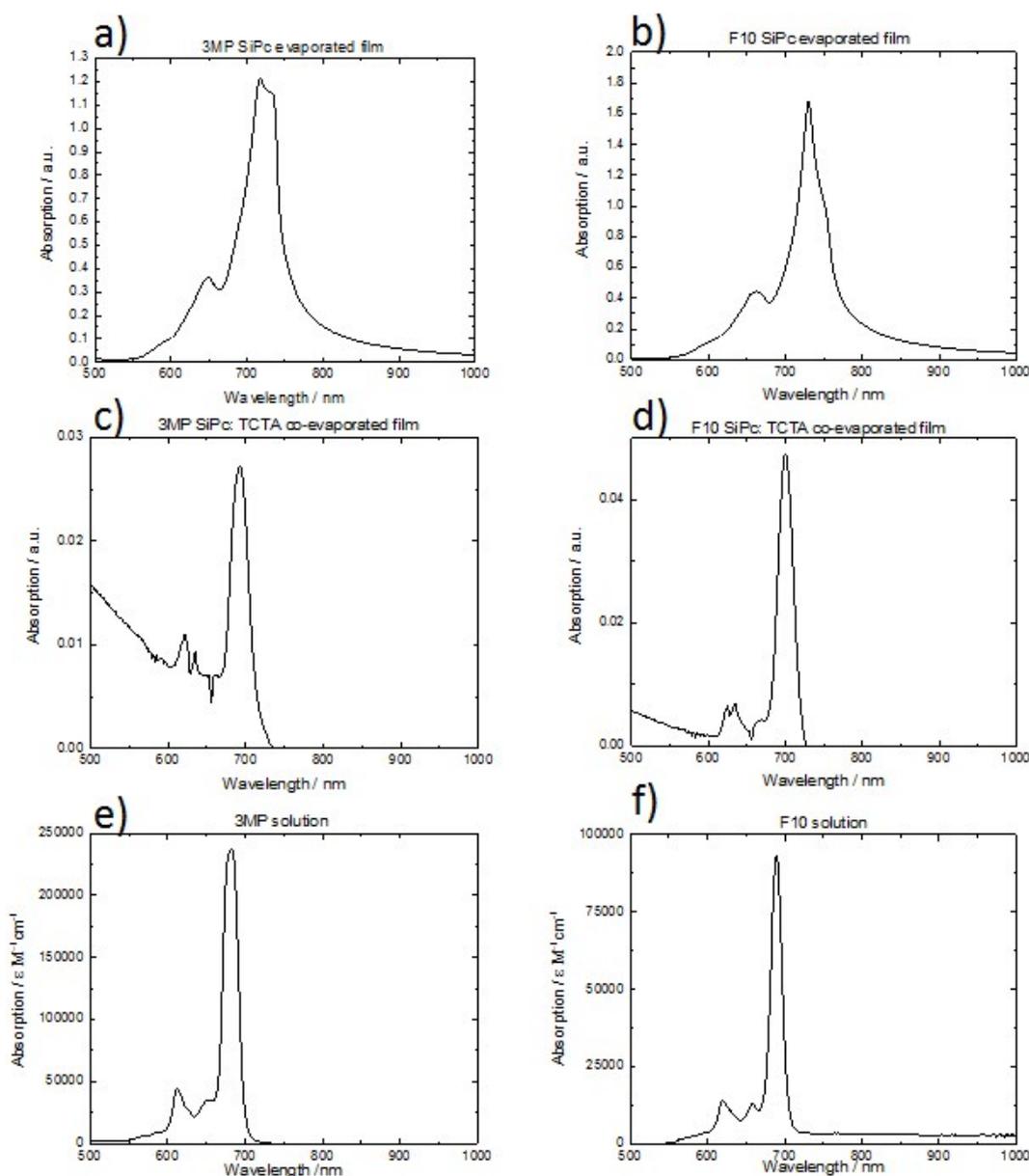


**Figure S8:** PL spectra measured for films of the two host materials used in optimised solution-processed and vacuum-processed OLEDs. TCTA was excited at 360nm and a 375nm long pass filter used. F8BT was excited at 405nm and a 435 nm long pass filter used.



**Figure S9:** PL from the  $(3MP)_2$ -SiPc and  $F_{10}$ -SiPc. Panels a), c) and e) show  $(3MP)_2$ -SiPc in evaporated pure film, co-evaporated TCTA blend film at 5% weight concentration and 0.001mg/ml solution in CB respectively. Panels b), d) and f) show the same preparations for the  $F_{10}$ -SiPc. Photoexcitation of the samples was as described in previous figures. It can clearly be seen that the colour purity and shape are maintained in the co-evaporated samples c) and d) compared to the solutions e) and f) supporting evaporation as a valid processing method for achieving a dilute non aggregated population. Panels a) and b) show a very different form, with a red shift of

the peak and additional IR features. The red-shifted emission (relative to a dilute solution) and enhanced features around 800 nm are attributed to aggregated phases of each phthalocyanine. Electronic transport and recombination in this phase seems unfavourable as this trend was not observed in the EL at higher weight concentrations of the guest.



**Figure S10:** shows the absorption data for the same samples as **Figure S9**. In addition to the form of the PL changing in the evaporated pure films, the shape of the absorption features in the purely evaporated film is also distinctly different to the dilute case extending further into the IR. If other forms of Pcs display this behaviour whilst retaining transport properties, this could be a mechanism for tuning absorption into the IR.

<b>Sample</b>	<b>Peak 1 (nm)</b>	<b>Peak 2 (nm)</b>	<b>Lifetime 1 (ns)</b>	<b>Lifetime 2 (ns)</b>
<b>3MP solution</b>	<b>688</b>	<b>NA</b>	<b>4.0</b>	<b>NA</b>
<b>3MP:F8BT film</b>	<b>562</b>	<b>697</b>	<b>3.1</b>	<b>NA</b>
<b>3MP:TCTA film</b>	<b>415</b>	<b>700</b>	<b>1.4</b>	<b>NA</b>
<b>3MP evap. film</b>	<b>738</b>	<b>800</b>	<b>3.6</b>	<b>0.53</b>
<b>F10 solution</b>	<b>690</b>	<b>NA</b>	<b>5.9</b>	<b>NA</b>
<b>F10:F8BT film</b>	<b>552</b>	<b>700</b>	<b>4.4</b>	<b>NA</b>
<b>F10:TCTA film</b>	<b>415</b>	<b>706</b>	<b>1.0</b>	<b>NA</b>
<b>F10 evap. film</b>	<b>755</b>	<b>820</b>	<b>6.3</b>	<b>0.43</b>
<b>F8BT</b>	<b>562</b>	<b>NA</b>	<b>3.6</b>	<b>NA</b>
<b>TCTA</b>	<b>417</b>	<b>530</b>	<b>1.5</b>	<b>4.2</b>

**Table S1:** Photoluminescence peak positions and lifetimes for the various samples studied in this work. The characteristics of the dilute solutions were chosen as a baseline for evidence of dispersed, non-aggregated SiPc populations in the host. As noted previously, the shorter lifetimes in the evaporated films are a result of a higher fluence used to excite these samples in the UV. For the TCTA-based samples photoluminescence was recorded used an ICCD with a  $\sim 4$  ns response time, indicating that any emission was not longer lived compared to the other samples.

Factor	3MP:F8BT	F10:F8BT
Number density	1.2	1
Transfer overlap	3.6	1
$1/r^6$	1.45	1
PLQE	1	2.6
Total effect	<b>2.41</b>	1

**Table S2:** Derivation of a predicted ratio between the photoluminescence intensity of (3MP)<sub>2</sub>-SiPc and F<sub>10</sub>-SiPc in F8BT:SiPc (99:1 wt%) blend thin films. Using an experimental-based model that accounts for guest number density, transfer overlap, nearest neighbour distance in a Förster Resonance Energy Transfer (FRET)-like regime and guest PLQE (in solution), a factor of 2.4 is calculated. This is in good agreement with the PL from the host guest films where there was 2.6 times more emission from (3MP)<sub>2</sub>-SiPc. The 7% difference will be a combination of the variation in spectral overlap in the solid state and any degree of aggregation in the films. In the model the guest molecules were assumed to form a cubic lattice. F8BT had a molecular weight of 150,000 g mol<sup>-1</sup> and a density of 750kg m<sup>-3</sup>.<sup>1</sup>

	Total	Host	Guest	Guest fraction
3MP:F8BT PL	308	56.7	252	0.82
3MP:F8BT EL	162	72.7	89.7	0.55
F10:F8BT PL	494	3396	155	0.31
F10:F8BT EL	93.8	8.41	85.4	0.91

**Table S3:** Comparison of the integrated luminescence values for the spectra presented in Figure 6, alongside the guest fractions.

	3MP:F8BT	F10:F8BT
PL prediction	2.4	1
PL guest fraction	2.6	1
EL guest fraction	1	1.65

**Table S4:** Comparison of the relative contributions by each dopant to the luminescence characteristics of F8BT:SiPc blend thin films. The values indicate that F<sub>10</sub>-SiPc must be acting 4.3 times more effectively as a trap site for excitons in the solution processed OLEDs to account for the differences between blend PL and device EL.

## References

1. B. Watts, P. Warnicke, N. Pilet and J. Raabe, *Physica Status Solidi (a)*, 2015, **212**, 518-522.