Tuning the colour and efficiency in OLEDs by using amorphous or

polycrystalline emitting layers.

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Electronic Supplementary Information

Electrochemistry

The redox properties of the target Pt(II) complexes were investigated by cyclic voltammetry. Unfortunately, the solubility of Pt(ppy)(2-PTZ) in CH_2Cl_2 , which is one of the preferred solvents for electrochemistry, is rather low, while the fluorinated analogue $Pt(F_2ppy)(2-PTZ)$ proved almost completely insoluble also in DMSO. Even though this feature limit the significance of the obtained results, it was possible to obtain a voltammetric curve for the complex Pt(ppy)(2PTZ) in CH_2Cl_2 by using a glassy carbon (GC) working electrode coupled to a Platinum counter and in the presence of a saturated calomelane electrode (SCE) as the reference. In the region of the positive potentials, a Pt(II)-based and electrochemically and, likely, chemically irreversible process that is roughly centered at 0.9 V is observed. Relative to reductions, the voltammetric wave consist of one electrochemically irreversible process centered at -1.8 V that is assigned to the formation of a ligand (ppy or 2-PTZ)-based radical anion.





Figure S1. Experimental - Cyclic voltammetries were carried out using a Autolab Type III potentiostat with computer control and data storage via GPES 110 Manager software. Solutions of concentration 1 mM in CH_2Cl_2 were used, containing $[Bu_4N][BF_4]$ as the supporting inert electrolyte. A three-electrode assembly was employed, consisting of a Glassy Carbon (GC) working electrode, platinum wire counter electrode and saturated calomelane (SCE) reference electrode. Solutions were purged for 5 min with solvent-saturated nitrogen gas with stirring, prior to measurements being taken without stirring.

OLED configuration



Figure S2. Architecture of the LEDs manufactured, and molecular structures of the materials used. These are completed with energy level diagram shown for understanding the exciton and electronic traffic within the devices. The highest occupied molecular orbital (HOMO) obtained for each material corresponds to its ionization potential. The lowest unoccupied orbital (LUMO) is equal to the molecular electronic affinity. The Fermi level positions for ITO and Al electrode contacts are added for completion. The positions of all the levels are indicated by the numbers in electronvolts relative to the vacuum level at energy zero. HOMO and LUMO levels (eV) as calculated from redox potentials.

Transient Decay Analysis



Figure S3. Room temperature transient PL decays from both [4 wt% Pt complex :TCTA] blends (a), from both [10 wt% Pt complex :TCTA] blends (b) , from both [20 wt% Pt complex :TCTA] blends (c) and from neat films of both Pt complexes (d) on the microsecond time scale after excitation using light pulses of duration 1ns at $\lambda_{exc} = 373$ nm. Also shown is the response time of the dimer phosphorescence from the neat films on a decimal nanosecond scale (inset) detected at $\lambda_{det} = 750$ nm. Open circles represent the experimental data and solid lines are decay fits. Single-photon IBH model 5000 counter were employed for the time resolved luminescence measurements.

X ray diffraction



Figure S4. Diffractogram of the starting bulk Pt(ppy)(2-PTZ). The powder is crystalline, the sharp peak at 2 θ = 16.3° is due to the sample holder.



Figure S5. Diffractogram of the starting bulk Pt(F2ppy)(2-PTZ).



Figure S6. Comparison of the diffractograms of: the as-deposited Pt(F2ppy)(2-PTZ) thin film (blue line), the thin film after heating at 160°C for 30 minutes (green line) and the starting crystalline powder (red line). The as-deposited Pt(F2ppy)(2-PTZ) thin film presents a strong peak at d=10.6 Å which is not present in the starting material, suggesting the formation of a new form. Upon

heating at 160°C the film converts into the bulk phase which can be easily detected by its colour change (from light yellow into pink) and confirmed by the presence of several peaks which correspond the starting powder structure.