

Supplementary information for

Plasmon Enhanced Fluorescence from Meticulously Positioned, Studied Gold Nanoparticles deposited by Ultra Sonic Spray Coating in Organic Light Emitting Diodes.

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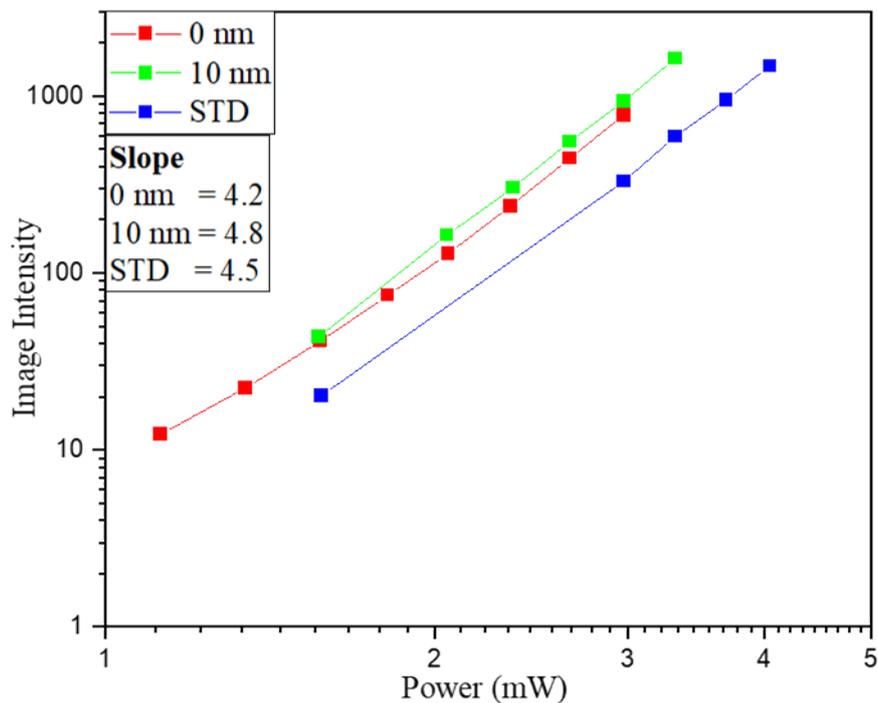
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Supplementary information 1

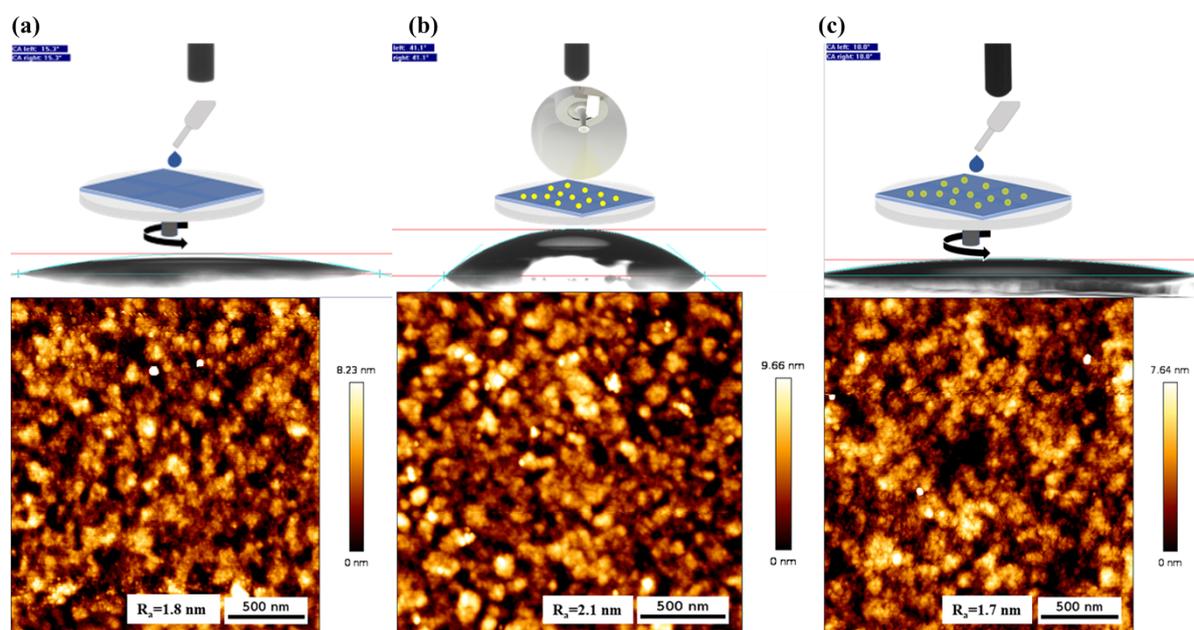
The 15 nm gold nanoparticles used in the present study are in a glass or PEDOT:PSS or Super yellow surrounding. The surface plasmon resonance of the gold nanoparticles is very sensitive to the dielectric properties of the surrounding medium, it is because a very small change of the refractive index in the proximity to the nanoparticles' surface may lead to significant shifts of plasmon resonance. Also, the surface plasmon resonance of the gold nanoparticles is dependent on the size and shape of the nanoparticles. Based on literature it is understood that 15 nm gold nanoparticles are big enough to have surface plasmon resonance at the emission wavelength where two-photon absorption takes place.

However, according to R A. Farrer et. al^[1], it is possible to conclude whether the absorption is multiphoton or not, by plotting the emission intensity vs the laser power. Once the absorption is established then, this is followed by the surface plasmon resonance. Therefore, for the present study, the logarithmic plot of the laser power versus emission intensity for the three different configurations of the substrates used for the measurements conducted is shown in supplementary figure 3. Here all three configurations show slopes above 2, which represents the multiphoton process^[1].



Supplementary figure 1: Multiphoton absorption intensity vs the excitation power for the different configurations of the substrates. The slopes for all three configurations represent multiphoton absorption.

Supplementary information 2



Supplementary figure 2: water contact angle and AFM surface morphology measurements for samples (a) Spin coated PEDOT:PSS, (b) Ultrasonically spray coated PSS stabilized gold nanoparticles (c) Spin coated PEDOT:PSS on PSS stabilized gold nanoparticles

To validate that there is no dissolving of the underneath PEDOT:PSS during layer by layer deposition, two sets of experiments were conducted

- (1) Water contact angle
- (2) Surface topography by AFM.

Supplementary Figure 2, explains the water contact angle and surface morphology by AFM for the steps (a) spin coated PEDOT:PSS, (b) Ultrasonic spray coated PSS stabilized gold nanoparticles (c) Spin coated PEDOT:PSS on top of PSS stabilized gold nanoparticles.

The water contact on the sample (a) and (c) is $\sim 15^\circ$ and 10° showing the affinity of the deposited PEDOT:PSS layer to attract water or the underneath PEDOT:PSS layers are dissolving, however with the sample (b) the water contact angle is 41° , this shows in comparison with the only PEDOT:PSS layers, the PSS stabilized gold nanoparticle layers are exhibiting less affinity towards water.

The AFM images for the samples (a), (b) and (c) show the surface roughness (RMS) of 1.8nm, 2.1nm and 1.7nm respectively. The slight increase in the RMS surface roughness value of sample (b) is due to the deposition of gold nanoparticles.

With both water contact and AFM measurements, it is clearly seen that due to the presence of PSS stabilised gold nanoparticles, upon layer-by-layer deposition of PEDOT:PSS, there is no dissolving of the underneath PEDOT:PSS layer.

Supplementary information 3

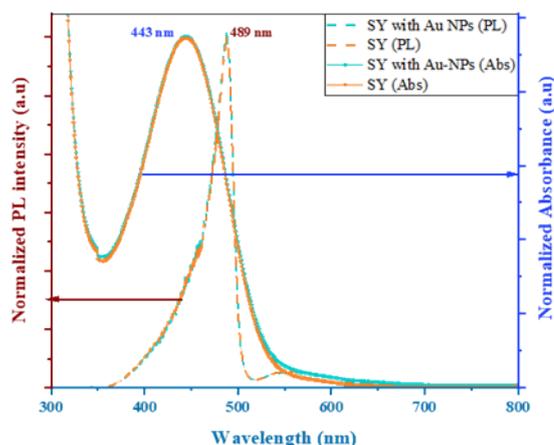
Photoluminescence quantum yield (PLQY) experiments on spin coated films have been performed using an integrating sphere (Thorlabs IS200-4) following the procedure described in ref^[2]. A high-radiance broadband light source (Energetiq, EQ99 LDLS) in combination with an appropriate band-pass filter was used for photo-excitation with blue light. The integrating sphere was connected with a CCD spectrograph (Avantes, Avaspec-3648) via an optical fibre (600 μm diameter). All spectra were corrected for the spectral response of the sphere and the detection system determined using a calibrated light source (Avantes, AvaLight-HAL-CAL-Mini). To avoid photodegradation during the experiment, the organic thin films were covered with a layer of polydimethylsiloxane to reduce oxygen diffusion to the illuminated area.

PLQY ($\pm 2\%$)

with NP's 5.9 %

without NP's 5.6 %

The observed 5% increment upon incorporating the nanoparticles is significantly less than the 2 order magnitude increase in the fluorescence intensity measured by the 2PF measurements. This could be explained on photo-chemical nature of the Super yellow polymer. For the photoluminescence quantum yield measurements, the samples were excited by blue light. It is known that PPV based polymers are susceptible to photobleaching in the blue light^[3]. This induces degradation of the polymer, which in turn reduces the density of fluorophores and hence the quantum yield. However, in the case of 2PF the photodamage is limited to a sub-femtolitre volume at the focal point^[4]. This reduces the photobleaching and hence increases the visibility of the fluorescent enhancement.

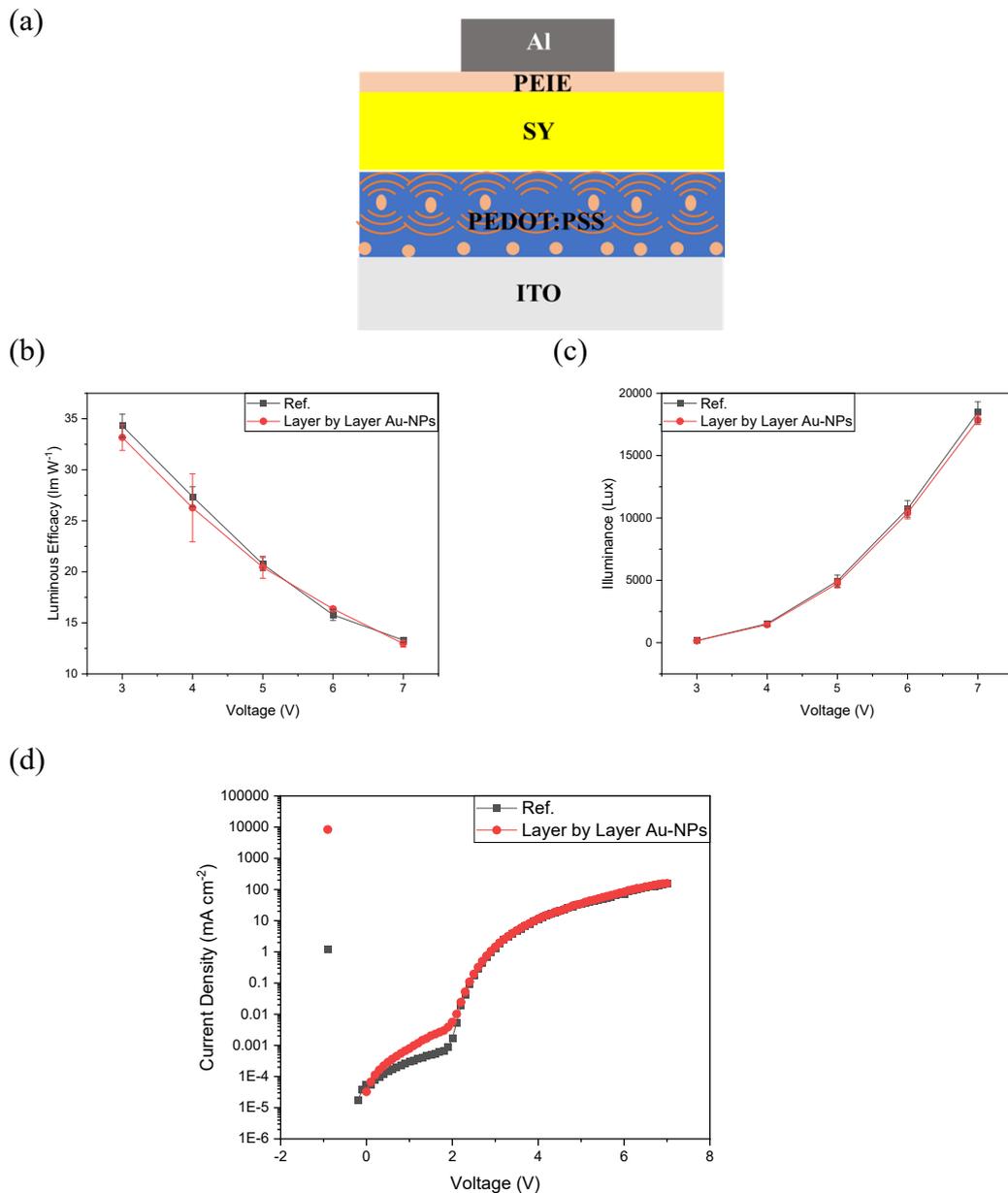


Supplementary figure 3: Normalized absorbance and photoluminescence of the OLEDs with and without Au-NPs.

As seen from the both PL and absorbance data, it is evident that there is no redshift or blueshift of the spectrum upon incorporating the Au-NPs. This is a clear indication that the nanoparticles are not acting as impurities or there is no change in the electronic structure of the sample. The plasmon enhanced absorbance is observed with a slight enhancement in the absorbance spectrum but not significant. However, the same cannot be said for the PL measurements. If there was any charge transfer and additional non radiative pathways, then the PL intensity of the Au-NPs incorporated devices would have reduced PL intensity^[5]. Thanks to the design of the vertical position of the Au-NPs compared to the fluorophore, these are eliminated. Also,

the PL intensity and absorbance depend on the density of the nanoparticle deposited. This might be suitable for the enhanced optical properties, but for devices, the presence of Au-NPs greater than a surface coverage of 2.1% would result in affecting the charge injection/transport properties. Therefore, in the present work, the surface coverage of $\sim 2\%$ was achieved using the USSC which is a trade-off between the optical and electrical properties of incorporating the Au-NPs in organic light emitting diodes.

Supplementary information 4



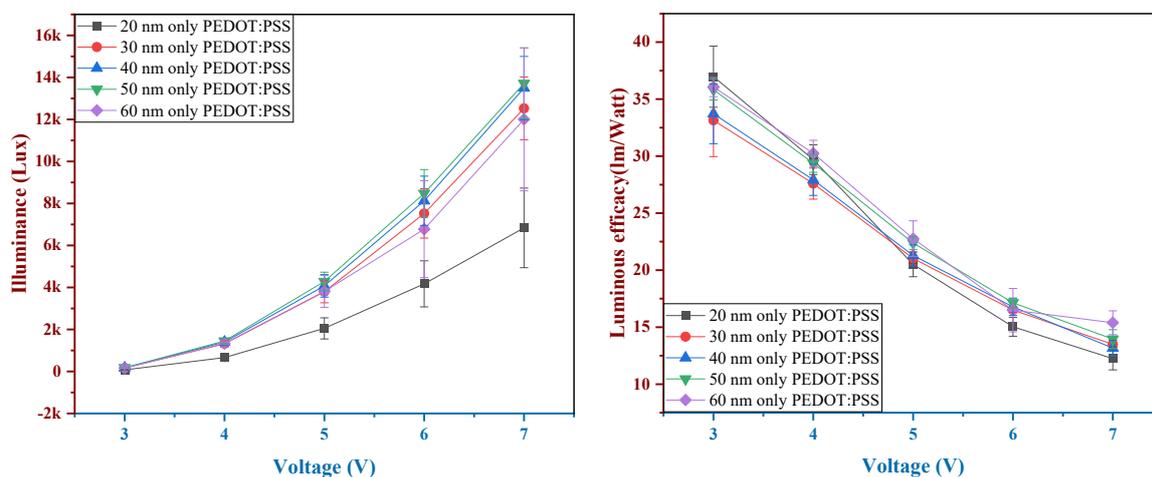
Supplementary figure 4: a) Architecture of the OLEDs incorporating layer by layer deposition of Au-NPs. Performance of the OLEDs. b) Luminous efficacy. c) illuminance. d) IV characterization for the devices built with layer-by-layer deposition of Au-NPs.

The layer-by-layer deposition of PNPs as shown in OLEDs architecture supplementary figure 4 a, is built to understand the influence of vertical field coupling of the PNPs over the OLED performance. With both the luminous efficacy (b) and illuminance (c), there is no increment in the OLED behaviour and no traces of far-field coupling, this is further explained by current density vs voltage characteristics. At low voltage the layer-by-layer deposited PNPs show an increased current density, this happens because of shunt resistance, the incorporated nanoparticle provides a close path for the charges to traverse through the PEDOT:PSS, this current density behaviour combined with field coupling of PNPs due to close proximity (figure 4 d) would result in a reduction of near field coupling of PNPs with the dipole of a fluorophore and hence no change in OLEDs performance.

Supplementary information 5

The conductivity of the PEDOT:PSS can be increased by increasing the thickness, however, with the increase in the conductivity the transparency of the PEDOT:PSS layer decreases. This results in decreasing the light outcoupling from the device and hence the efficiency.

To confirm the obtained results are not due to the thickness of the PEDOT:PSS, we built five sets of devices where the thickness of the PEDOT:PSS is varied (20, 30, 40, 50 and 60nm).

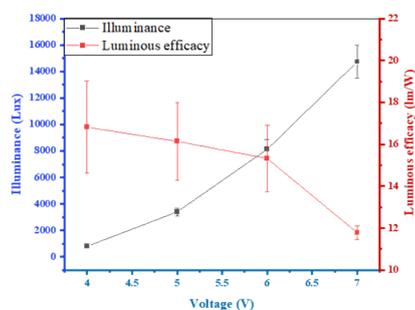


Supplementary figure 5: Light emission characteristics of the OLEDs with different thickness of PEDOT:PSS

As can be seen from supplementary figure 5, the best performing device considering both the illuminance and the luminous efficacy is the 40 nm PEDOT:PSS. This proves that the observed enhancement in the OLEDs performance of the Au-NPs incorporated devices is due to plasmon enhancement rather than the thickness.

Supplementary information 6

The conductivity of the PEDOT:PSS could be increased by surface treatments^[6] like chemical



treatment, thermal treatment, plasma treatment and ozone treatment.

Figure 1. OLED light emission performance parameter for the PEDOT:PSS/IPA/PEDOT:PSS stack.

Chemical treatment like alcohol treatment increases the active species so that the mobility of the charge carrier increases significantly. In our experimental procedure, we deposited the Au-NPs dispersed in the IPA solvent utilizing the ultrasonic spray coating (USSC). The droplets generated by the USSC are ~20 micrometers^[7]. The flow rate is ~0.3ml/min. Substrate temperature of 30 degrees Celsius. At this very low flow rate and the substrate temperature, by the time the droplets reach the substrate, the IPA is evaporated and leaving the deposition of PSS stabilized Au-NPs only on the substrate. This reduces the possibility of any IPA treatment of the PEDOT:PSS to the minimum.

To prove this, we have performed a blank experiment where the solvent system without the Au NP is sprayed with the same conditions. Results show that, figure 1 the maximum efficacy of the devices achieved is 20 lm/W, whereas the plasmon incorporated devices exhibited 37 lm/W. This shows that the observed OLEDs performance enhancement is due to the plasmon enhancement

Reference

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