Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Organic Plasmonics: PEDOT Nanoparticles are Getting Closer to the Visible Range

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Supporting Information

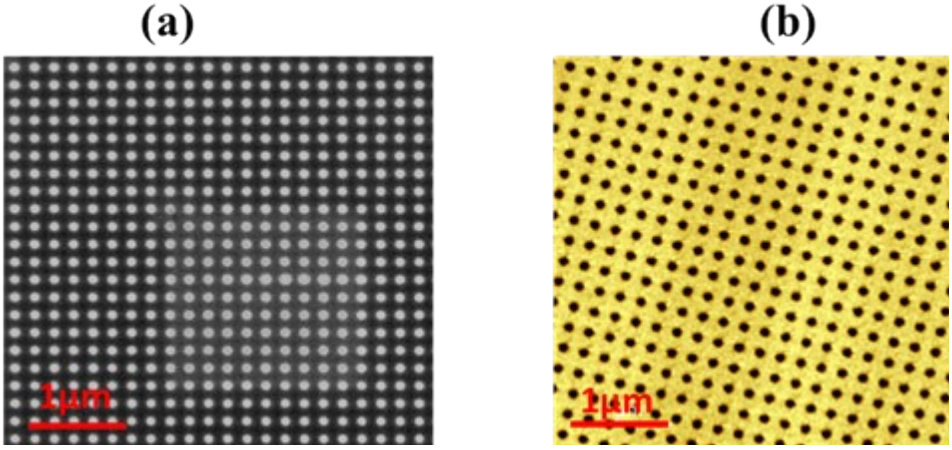

Figure S1: (a) SEM image of nanoholes and (b) AFM image of nanoholes of 120 nm diameter in PMMA after the development process. The method was explained in a previous publication [1]. Both images demonstrate the homogeneity of the geometry.

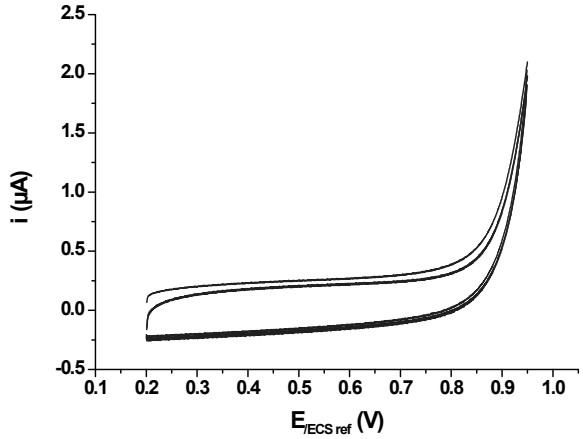

Figure S2: Electropolymerization of PEDOT/DS on ITO/PMMA with nanoholes in aqueous electrolyte, [$LiClO_4$]=0.1 M, [EDOT]=5 mM, [SDS]=0.07 M. The scan rate is 0.1V/s and the potential is swept in 3 cycles from 0.2 V to 0.95 V. The counter-electrode is a stainless steel grid.

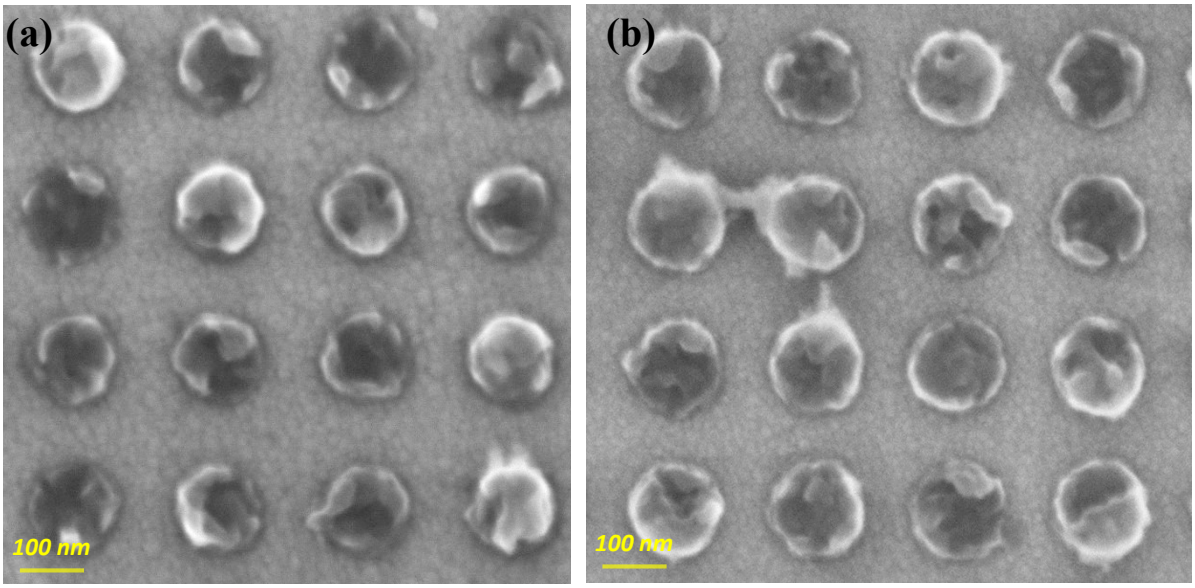

Figure S3: (a) SEM image of PEDOT/DS NPs of 120 nm and (b) 150 nm diameters after electrodeposition of PEDOT/DS by cyclovoltametry in aqueous solvent. The sample was rinsed with distilled water and dried before characterization.

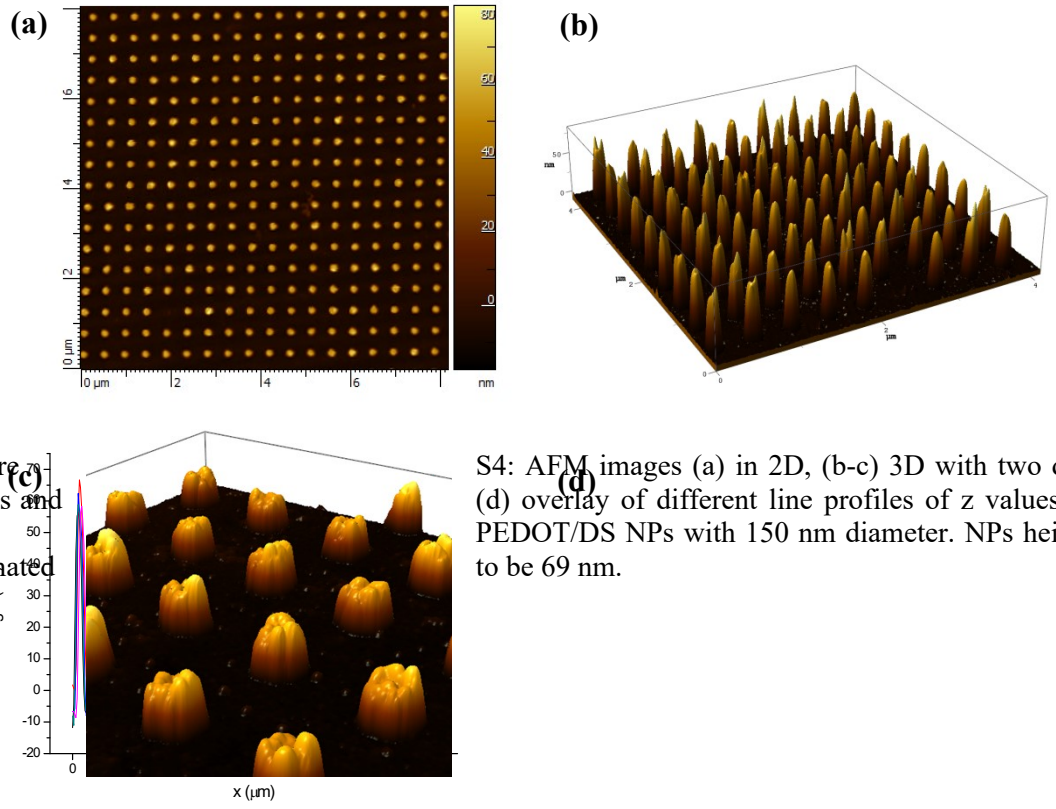

Figure S4: AFM images (a) in 2D, (b-c) 3D with two different views and (d) overlay of different line profiles of z values for the estimated PEDOT/DS NPs with 150 nm diameter. NPs heights are to be 69 nm.

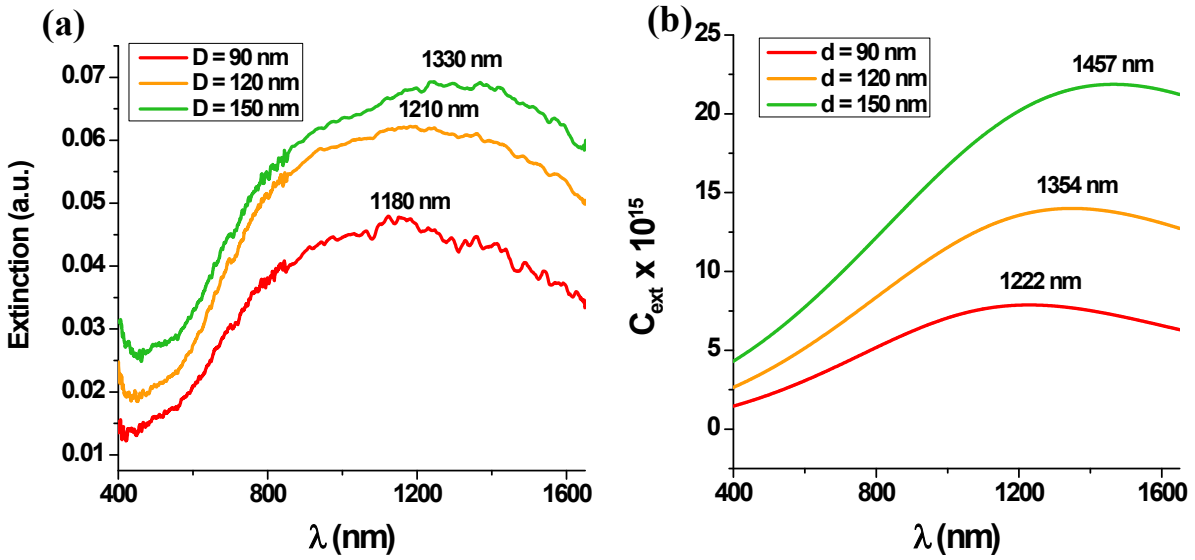

Figure S5: (a) Extinction spectra of nano-disks (height h = 60 nm) of PEDOT/DS of different diameters (90nm -red curve, 120 nm-yellow curve and 150 nm-green curve) (a) experimental spectra (b) Simulated extinction factor with $plasma\ frequency\ \omega_p = 2.0\ eV$ and $relaxation\ time\ \tau = 0.5\ fs$

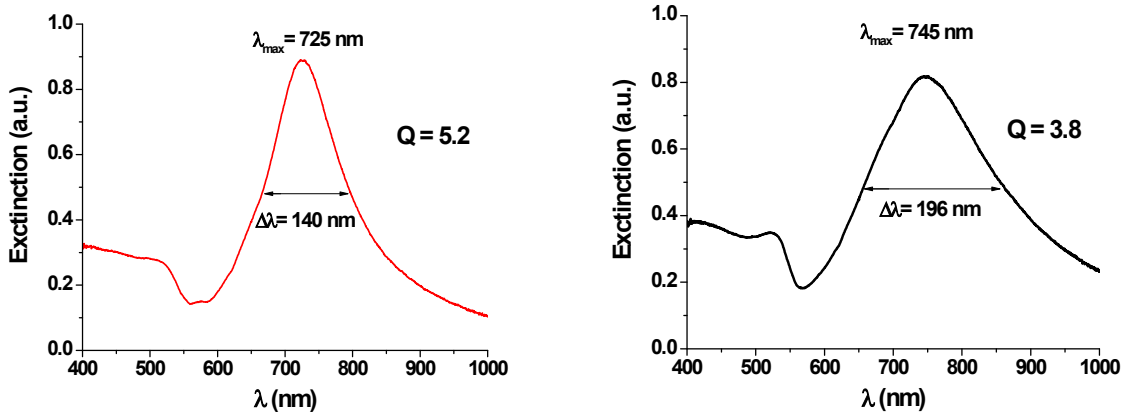

Figure S6: Extinction spectra of gold NPs arrays with NPs of diameter of 210 nm (red) and 240 nm (black) with a grating constant of 360 nm and 50 nm height prepared by lithography [1] on ITO substrate. Quality factors $Q = \lambda_{max}/\Delta\lambda$ were calculated for these two surfaces.

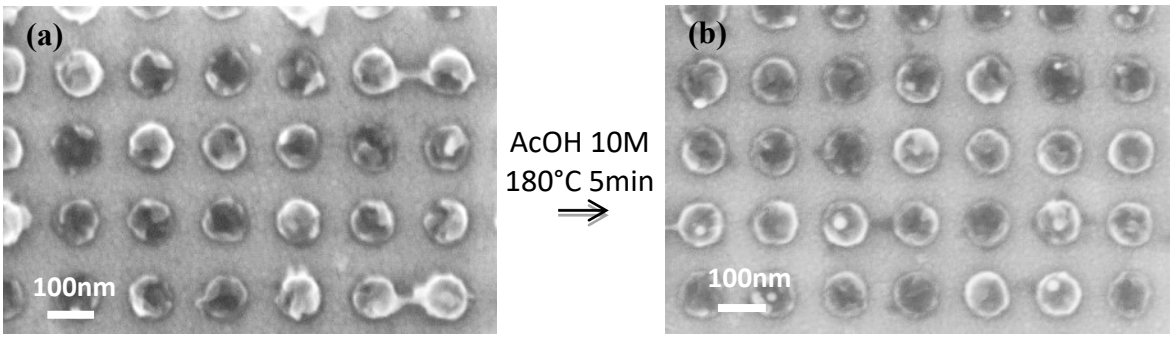

Figure S7: SEM of PEDOT/DS NPs of 90 nm diameter before and after acid treatment. The PEDOT/DS NPs were prepared using a 5 nm thick adhesion layer of oligo(bisthienylbenzene) (BTB) deposited by diazonium grafting to enhance the adhesion to the ITO substrate. (2) Secondary doping without BTB layers led to the destruction of the NPs. A 20 µL droplet of 10 M acetic acid in water was placed on the PEDOT/DS NPs arrays and heated at 180 °C for 5 min. The surface was then rinsed with distilled water and dried with argon. The SEM images show that NPs remain on the surface after the acid treatment and that their geometry is unchanged.

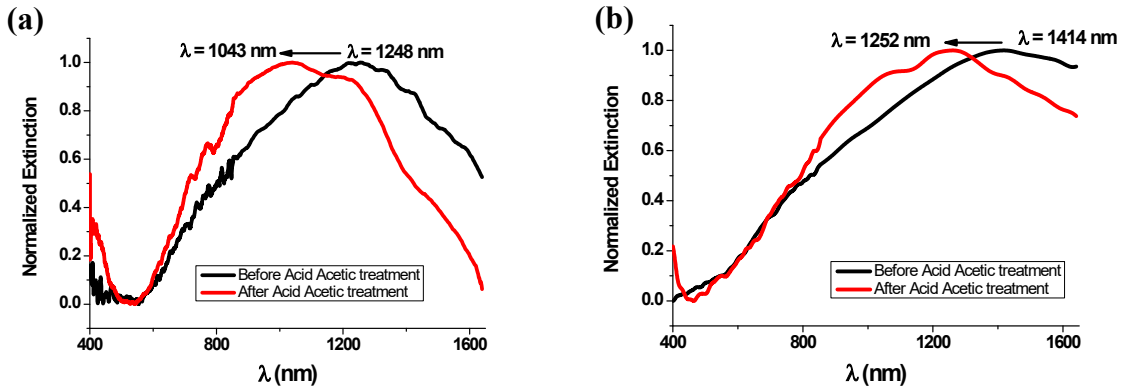

Figure S8: Normalized extinction spectra of PEDOT NPs before (black curve) and after (red curve) acid treatment. (a) diameter 120 nm, height 40 nm (b) diameter 240 nm and height 40 nm.

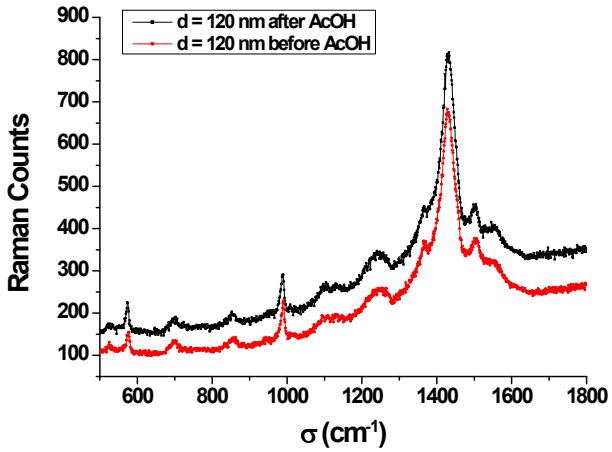

Figure S9: Raman spectra of PEDOT NPs before (red) and after (black) acid acetic treatment. Excitation wavelength is 633 nm and acquisition time of 3*10 s. The diameter of the Nps is 120 nm.

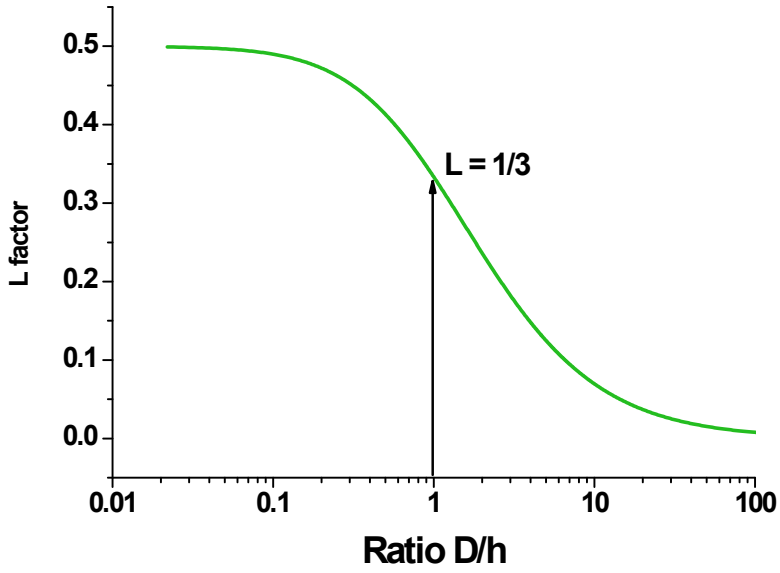

Figure S10: calculation of L for different d/h ratio. L factor value is 1/3 when d/h=1 (it is the particular case of a NP sphere), approaches L=0.5 for high h compared to d and L=0 for high d compared to h (case of thick film, no LSPR behaviour).

$$L = \frac{r^2 h}{4} \int_0^{\infty} \frac{dq}{(r^2+q) f(q)} \; with \; f(q) = (r^2+q)\sqrt{(\frac{h_2}{4}+q)}$$

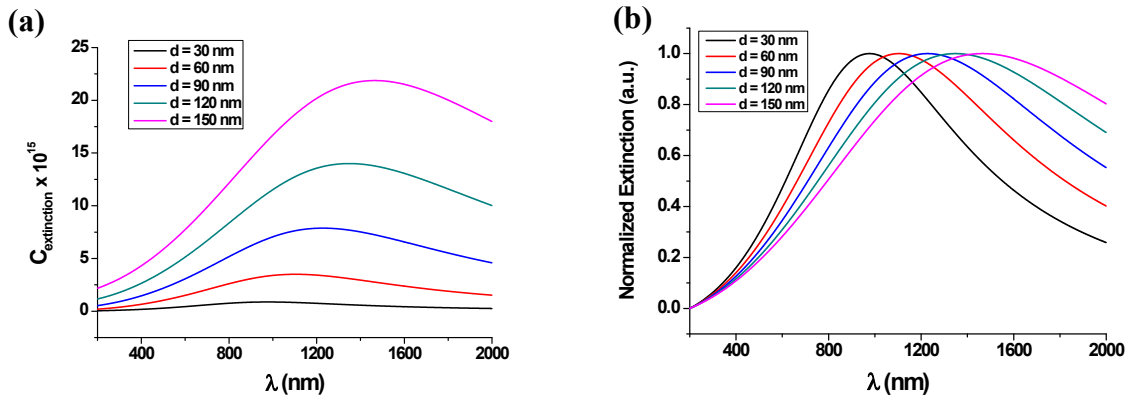

Figure S11: Extinction spectra of nano-disks (height $h = 60$ nm) of PEDOT for different diameters with $plasma\ frequency\ \omega_p = 2.0\ eV$ and $relaxation\ time\ \tau = 0.5\ fs$. a) non-normalized and (b) normalized spectra.

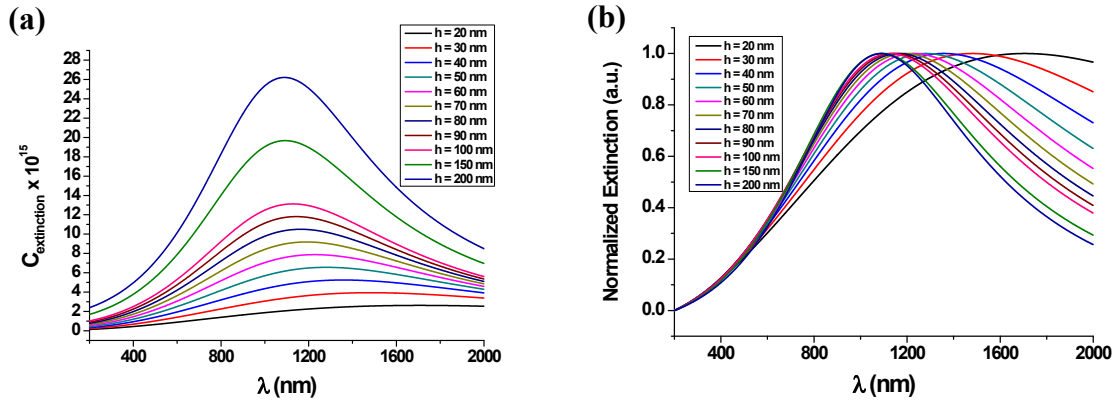

Figure S12: Extinction spectra of nano-disks (diameter $d = 90$ nm) of PEDOT for different heights with $plasma\ frequency\ \omega_p = 2.0\ eV$ and $relaxation\ time\ \tau = 0.5\ fs$. a) non-normalized and (b) normalized spectra.

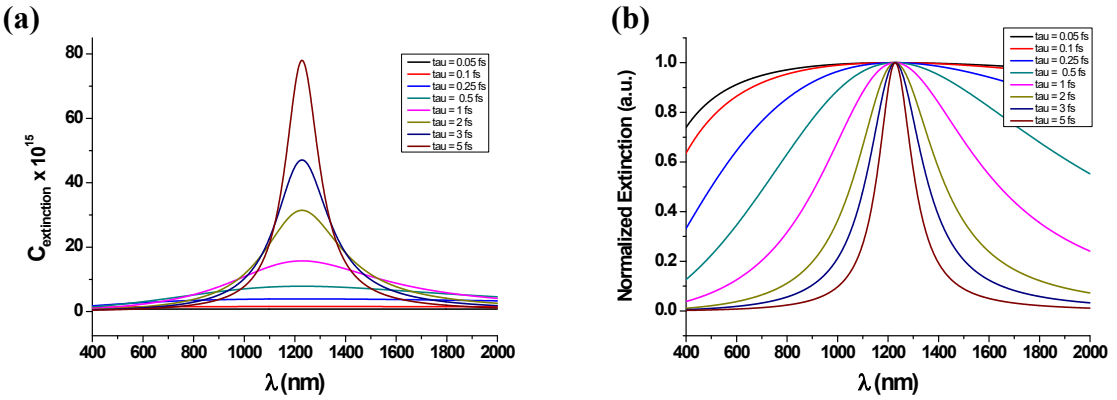

Figure S13: Extinction spectra of nano-disks (diameter $d = 90$ nm, height $h = 60$ nm,) of PEDOT for different relaxation time $\tau\ with\ plasma\ frequency\ \omega_p = 2.0\ eV$ (a) non-normalized and (b) normalized spectra.

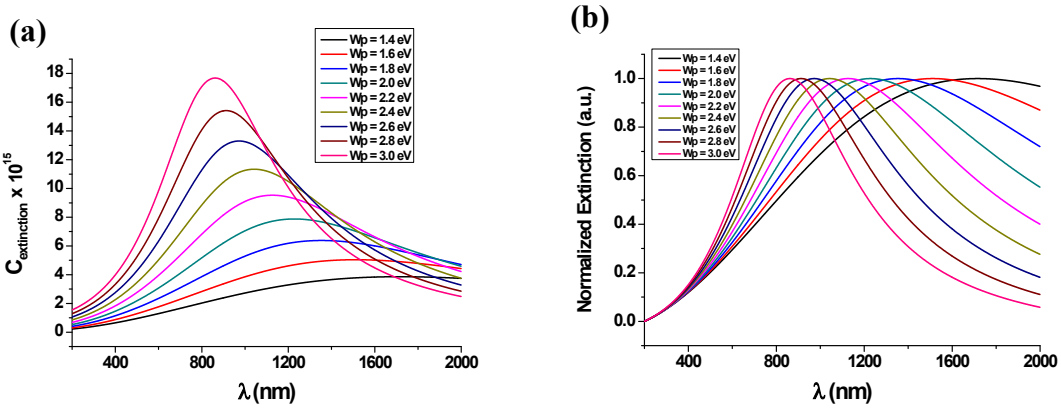

Figure S14: Extinction spectra of nano-disks (diameter $d = 90$ nm, height $h = 60$ nm,) of PEDOT for different plasma frequencies $\omega_p\ with\ relaxation\ time\ \tau = 0.5\ fs.$ (a) non-normalized and (b) normalized spectra.

References SI:

[1] P. Bléteau, M. Bastide, S. Gam-Derouich, P. Martin, R. Bonnet, and J. C. Lacroix, Plasmon-Induced Grafting in the Gap of Gold Nanoparticle Dimers for Plasmonic Molecular Junctions," *ACS Appl. Nano Mater.*, 2020, **3,** 8, 7789–7794,

[2] E. Villemin, B. Lemarque, T. T. Vũ, V. Q. Nguyen, G. Trippé-Allard, P. Martin, P.-C. Lacaze and J.-C. Lacroix, Improved adhesion of poly (3, 4-ethylenedioxythiophene)(PEDOT) thin film to solid substrates using electrografted promoters and application to efficient nanoplasmonic devices, *Synth. Met.*, 2019, **248**, 45–52.