

MOLECULAR PLASMONICS

Supplemental Information

Adam Lauchner,^{1,6} Andrea E. Schlather,^{2,6}* Alejandro Manjavacas,^{3,6}* Yao Cui,^{2,6}* Michael J. McClain,^{2,6} Grant Stec,^{2,6} F. Javier García de Abajo,^{4,5} Peter Nordlander,^{1,3,6} and Naomi J. Halas^{1,2,3,6}*

¹Department of Electrical and Computer Engineering, Rice University, Houston, TX, USA

²Department of Chemistry, Rice University, Houston, TX, USA

³Department of Physics and Astronomy, Rice University, Houston, TX, USA

⁴ICFO-Institut de Ciències Fòniques, Mediterranean Technology Park, 08860 Castelldefels (Barcelona), Spain

⁵ICREA-Institució Catalana de Recerca i Estudis Avançats, Passeig Lluís Companys, 23, 08010 Barcelona, Spain

⁶Laboratory for Nanophotonics, Rice University Houston, TX, USA

* Author contributions:

These Authors contributed equally to this work.

Correspondence and requests for materials should be addressed to N.J.H. (email: halas@rice.edu).

Electrochemical Measurements	2
Spectroscopic Measurements.....	4
Electrochemical Endurance.....	6
Electrochromic Device Spectrum.....	7
References	8

Electrochemical Measurements

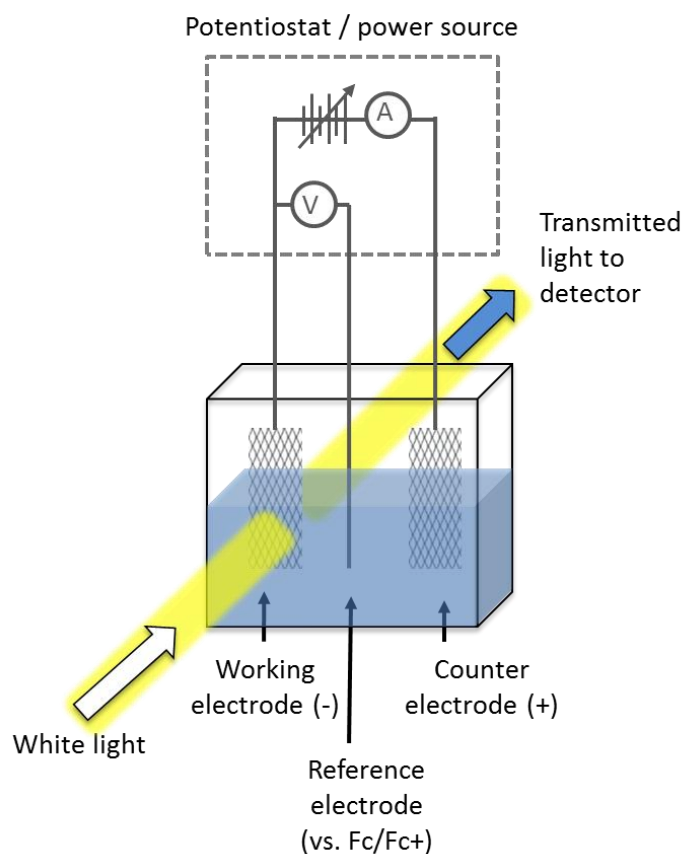


Figure S1: Spectroelectrochemical Setup. A three-electrode electrochemical cell configuration forms a complete circuit, controlled by potentiostat. White light is transmitted through the working electrode and recorded by a spectrometer. For the measurements conducted in this manuscript, the working electrode was always set as the negative voltage. The solution in the cell consists of 500 mM supporting electrolyte and 5mM PAH molecule in a dry organic solvent purged with argon.

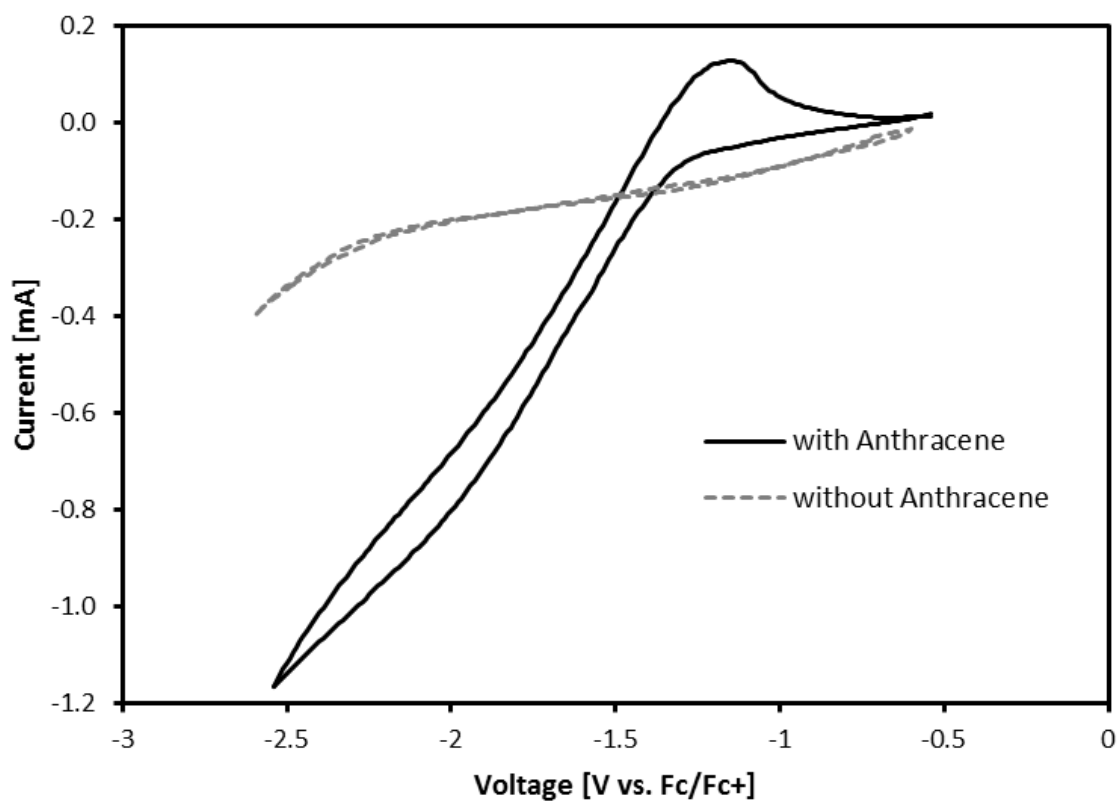


Figure S2: Cyclic Voltammogram. Current measured as a function of voltage sweep for THF (with 500 mM TBAP) both with 5mM Anthracene (solid, black line) and without Anthracene (dashed, grey line).

Spectroscopic Measurements and Simulations

The shape of the absorption band in tetracene above ~ 2.75 eV in Figure 2b is unreliable due to the concentration of the neutral solution. The HOMO-LUMO transition is strongly absorbing, resulting in low transmission at that energy for a 5mM solution with a 10mm optical path length and a weak, noisy signal for the anion when the neutral spectrum was subtracted from the total measured spectrum. Also, the apparent discrepancy between the heights of the neutral and anion peaks for tetracene compared to theory is due to the differences in concentration between the anion and the neutral molecule (concentration of anion was much lower than the concentration of the neutral molecule). The diffusion length around the electrode is much less than the 10mm optical path length; thus, even when the electrode was saturated with charged molecules, only a small fraction of the total molecules along the optical path were charged.

On the theory side, it has been shown that TDDFT calculations of the absorption spectrum of PAHs are limited to an accuracy of few tens of meV on the resonance peak positions when compared to experimental data.¹⁻³ Further, the spectra shown in Figure 2c do not include the fine detail due to vibrational coupling, which is expanded in greater detail in Figure 3, and which results in an excellent agreement between theory and experiment.

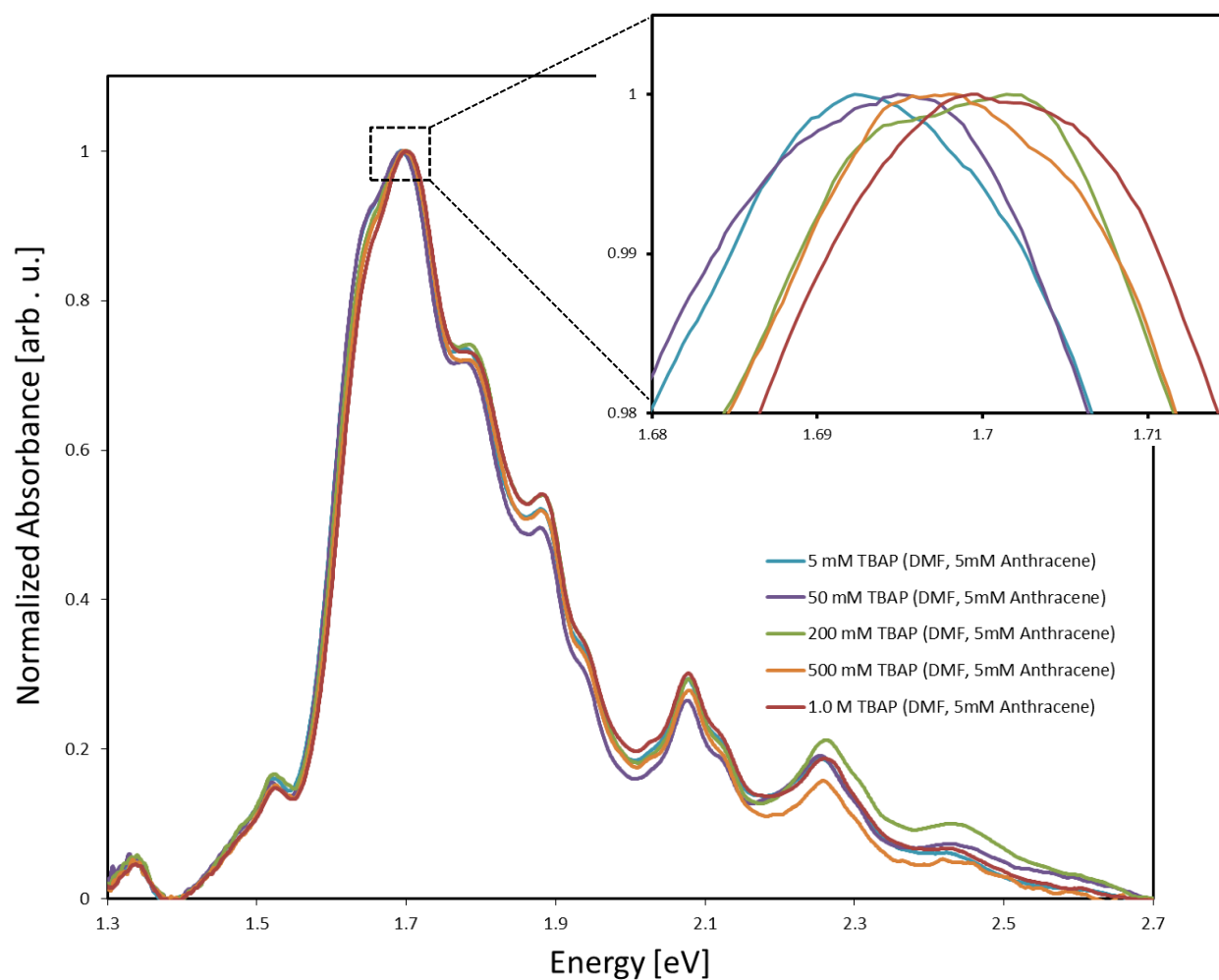


Figure S3: Electrolyte Concentration. The electrolyte concentration was varied from 5mM to 1,000 mM at constant Anthracene concentration (in DMF). While the system response is slightly slower at lower electrolyte concentration, the energy of the peak resonance redshifts only very slightly with increasing concentration.

Electrochemical Endurance

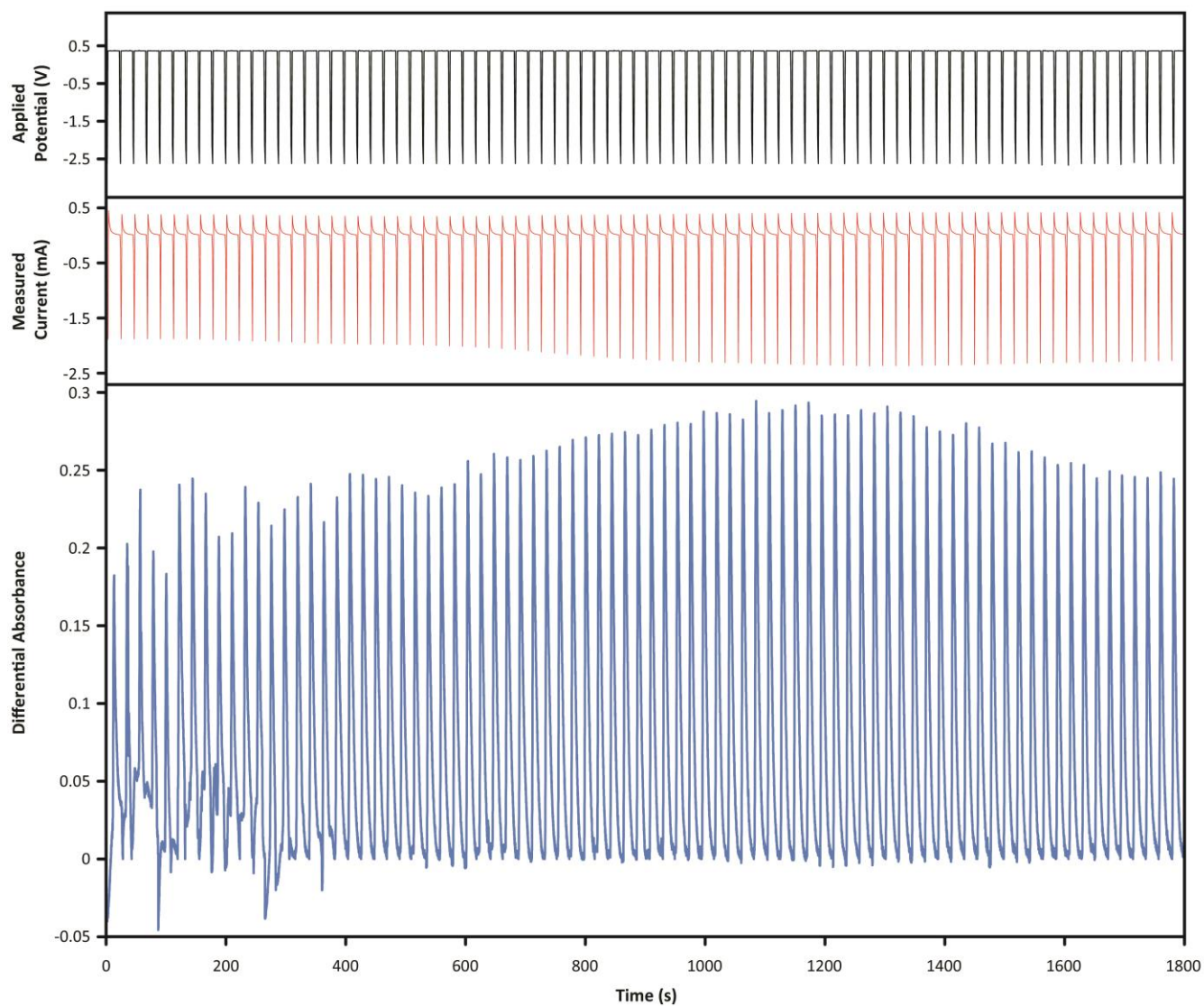


Figure S4: Plasmon switching endurance in electrochemical cell. A 10 mM Anthracene solution (in THF, 500 mM TBAP) was monitored spectroscopically during alternating applied voltages of -2.6 V for 3s and 0.4 V (vs. Fc/Fc⁺) for 20 seconds, over the course of 30 minutes. The differential absorbance during this period is plotted as measured at 1.71 eV (i.e., at the peak resonance of the molecule plasmon in Anthracene).

Electrochromic Device Spectrum

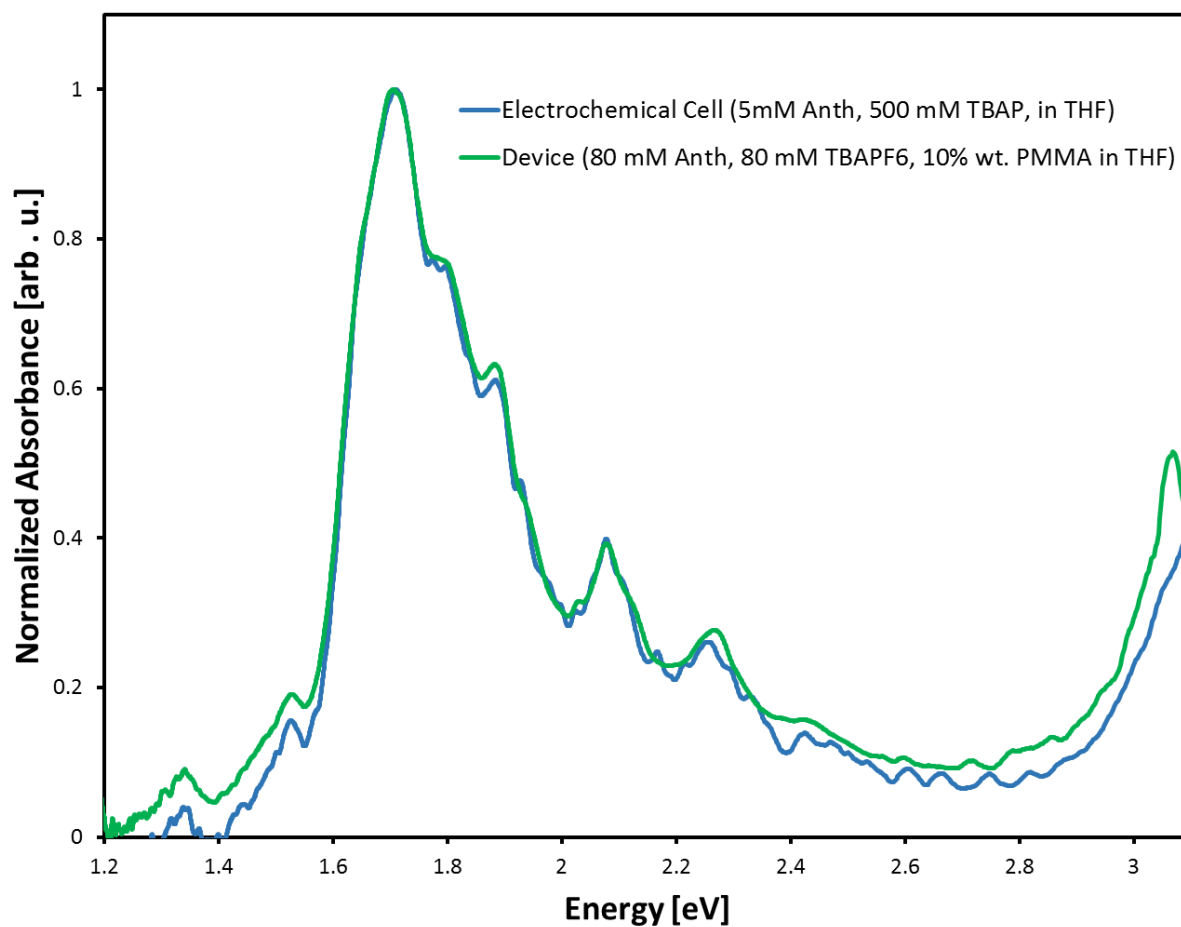


Figure S5: Comparison of solution-state and gel device molecular plasmon spectra.

Normalized absorption spectra of the anthracene anion molecular plasmon as recorded in solution with the electrochemical cell (blue curve) and the ITO-anthracene gel-ITO device.

References

1. Dominikowska, J., Domagala, M. & Palusiak, M. UV-vis spectra of singlet state cationic polycyclic aromatic hydrocarbons : Time- dependent density functional theory study UV-vis spectra of singlet state cationic polycyclic aromatic hydrocarbons : Time-dependent density functional theory study. **044324**, (2014).
2. Malloci, G., Cappellini, G., Mulas, G. & Mattoni, A. Electronic and optical properties of families of polycyclic aromatic hydrocarbons: A systematic (time-dependent) density functional theory study. *Chem. Phys.* **384**, 19–27 (2011).
3. Malloci, G., Mulas, G., Cappellini, G. & Joblin, C. Time-dependent density functional study of the electronic spectra of oligoacenes in the charge states -1 , 0 , $+1$, and $+2$. *Chem. Phys.* **340**, 43–58 (2007).