

### Captions

**Fig. 1.** Typical TEM image and UV-Vis spectra of (a) TAS-NPs, TEM taken at 75,000x magnification; (b) Ag-NPs, TEM taken at 25,000x magnification; and (c) Au-NSs, TEM taken at 60,000x magnification. The bars in the lower right corners of the TEM images represent 100nm. [Note: Histogram analysis of TEM imaging is included in the Electronic Supporting Materials (ESM), Graphic 1]

**Fig. 2.** (A) Comparison of poly-L-lysine (PL) linked NP films, showing differences in growth dynamics between low (LMW), medium (MMW), and high (HMW) molecular weight PL; (B) Comparison of poly(allylamine) hydrochloride (PAH) linked NP films, showing differences in growth dynamics between high MW PAH (MW ~70,000) and low MW PAH (MW ~15,000); (C) Comparison of poly(amidoamine) dendrimer (PAMAM) linked NP films, showing differences in growth dynamics between dendrimer generations 0.0, 1.0, 2.0 and 3.0; **Insets (A-C):** UV-Vis spectra of film growth with HMW PL, PAH, and PAMAM (G3.0), monitored every 2 dip cycles.

**Fig. 3.** (A) Comparison of various poly-L-Lysine (PL) linked NP films, showing differences in growth dynamics between single bridge linked, PL/PSS/PL linked, and PL/PSS/PL/PSS/PL linked constructions; (B) UV-VIS spectra showing SPB of final dip PL, PL/PSS/PL and PL/PSS/PL/PSS/PL multilayer TAS-NP films compared to TAS-NP solution. Absorbance values in solution and film spectra are not indicative of stability but rather differences in concentration.

**Fig. 4.** UV-Vis spectra showing the SPB of (1) PL linked TAS-NP films, (2) PL/PSS/PL linked films, and (3) PL/PSS/PL/PSS/PL linked films, both (a) in solution and (b) after exposure to air.

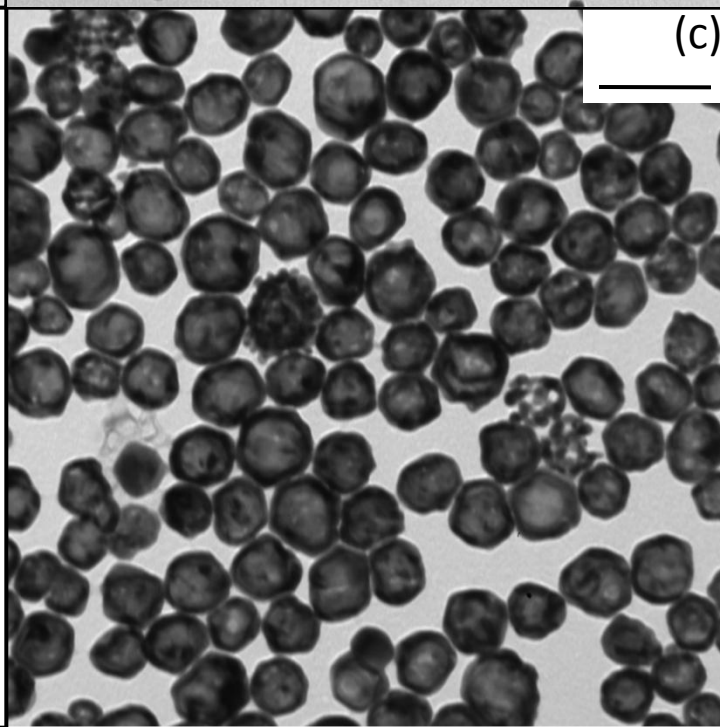
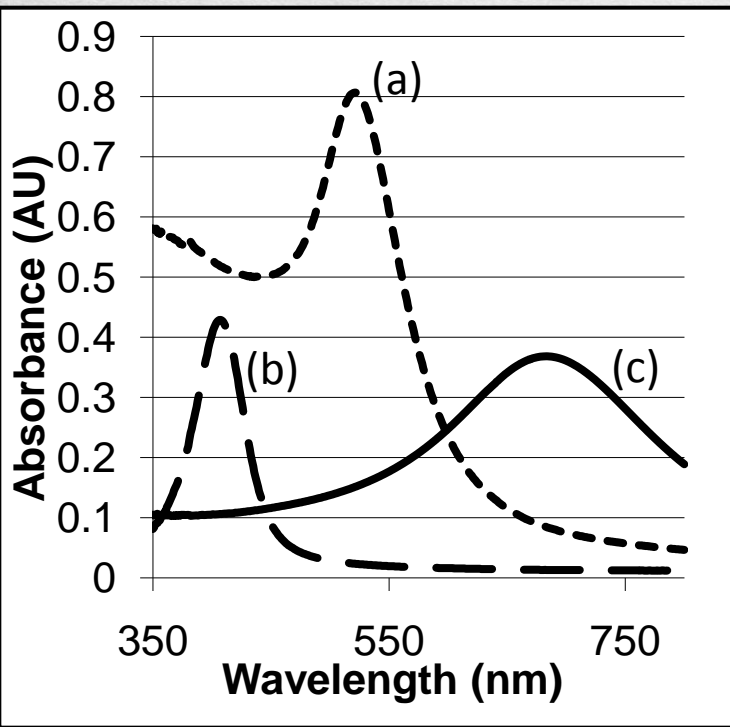
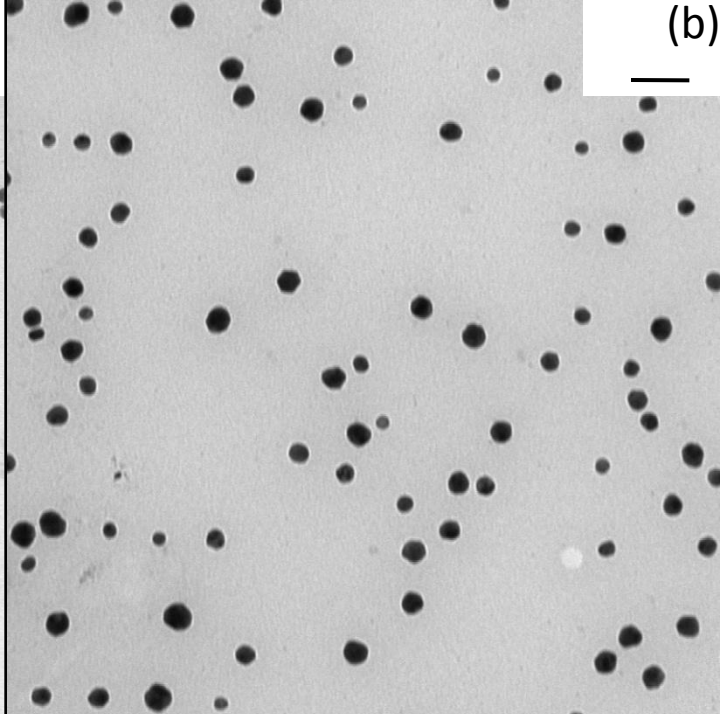
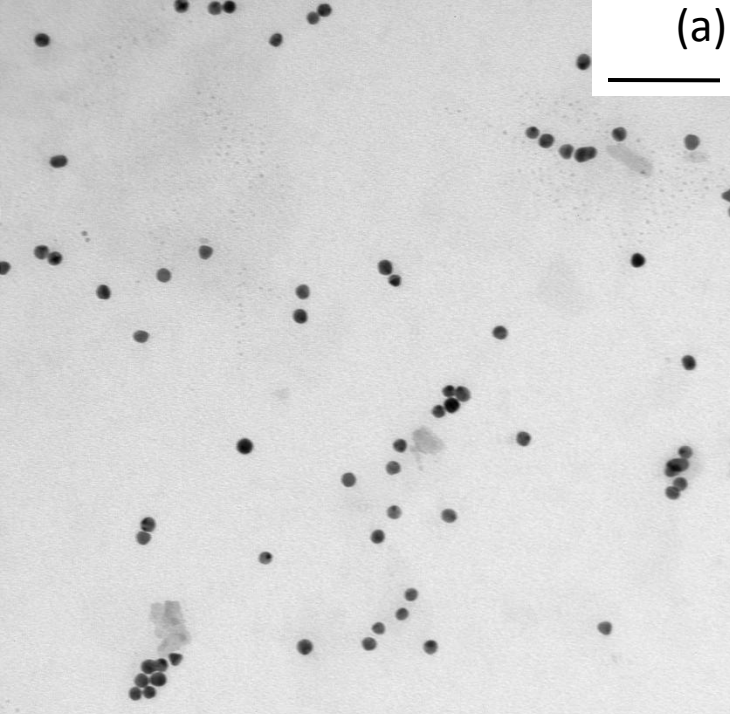
**Fig. 5.** (A) Comparison of PL/PSS/PL/PSS/PL linked film constructions of NPs versus NSs. **Inset:** UV-Vis spectra of NS film growth monitored every 2 dip cycles; (B) UV-Vis spectra showing SPB of (a) NS film in solution, (b) NS film after exposure to air, and (c) a solution of NSs provided for comparison.

**Fig. 6.** Changes in the  $\lambda_{\max}$  of the SPB for solutions of NPs (solid symbols) and NSs (open symbols) as a function of the  $\omega$ -substituted alkanethiol chainlength (i.e., methylene units, n) and terminal functional groups (-CH<sub>3</sub>, -OH, -COOH, 15-crown-5).

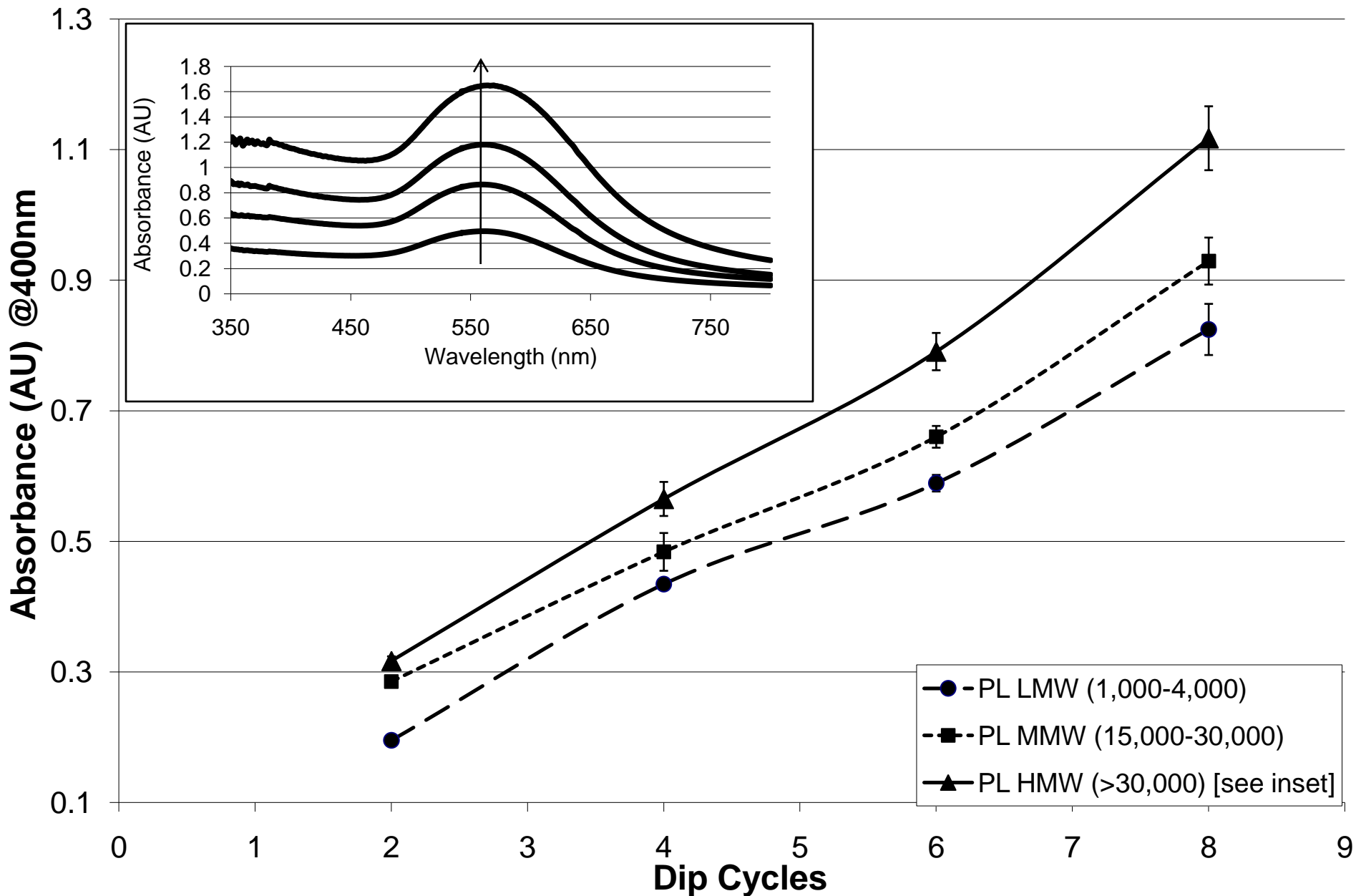
**Fig. 7.** UV-vis spectra showing SPB of NP film (A and C) and NS films (B and D) before and after exposure to butanethiol (**top**) and tetradecanethiol (**bottom**).

**Scheme 1.** Basic TAS-NP multilayer film with electrostatic bridge linked construction and various electrolyte and dendrimer linking materials used in film assembly.

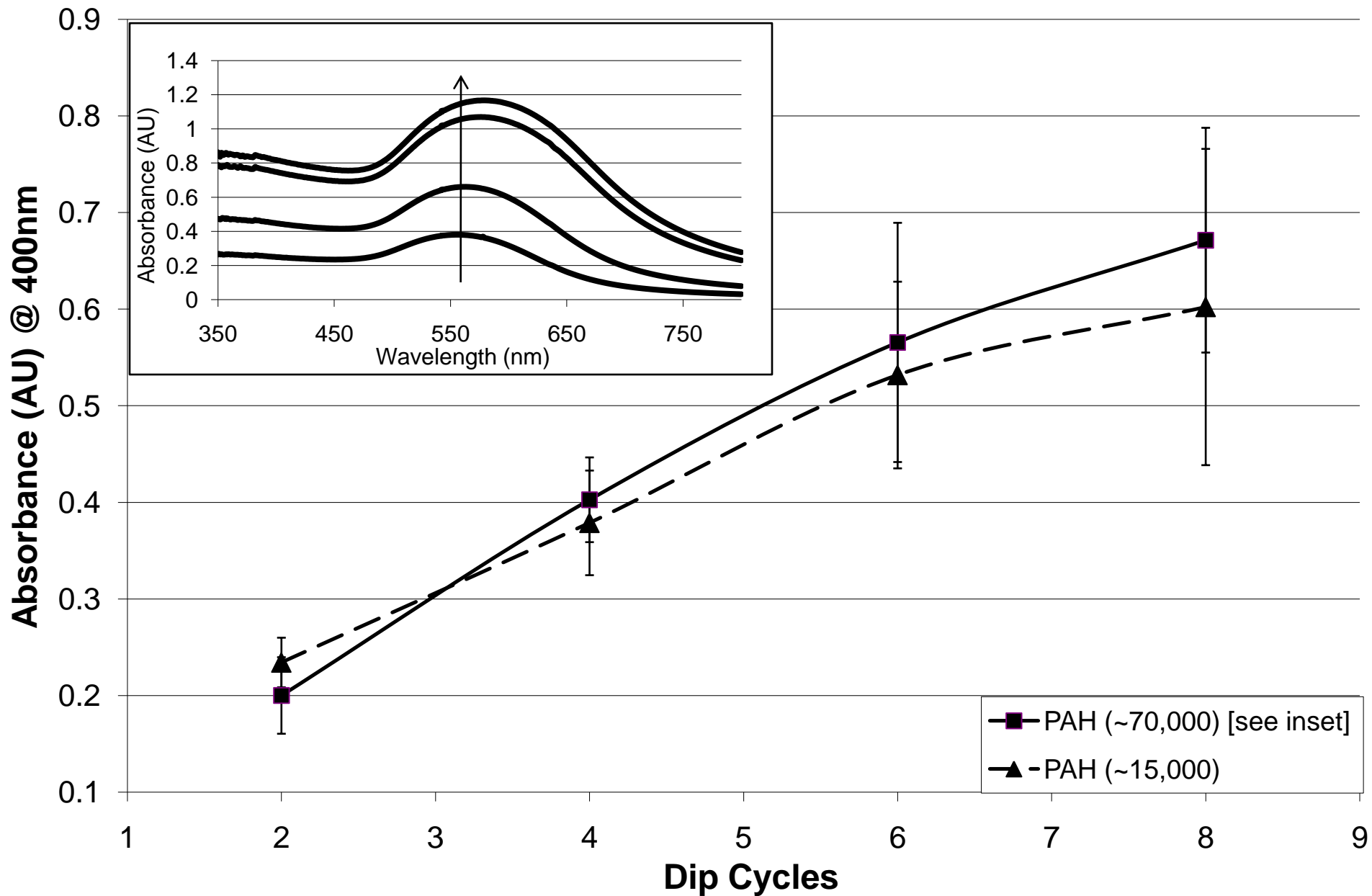
**Scheme 2.** Shows PL/PSS/PL/PSS/PL linked TAS-NP film construction. Film material not shown at scale.



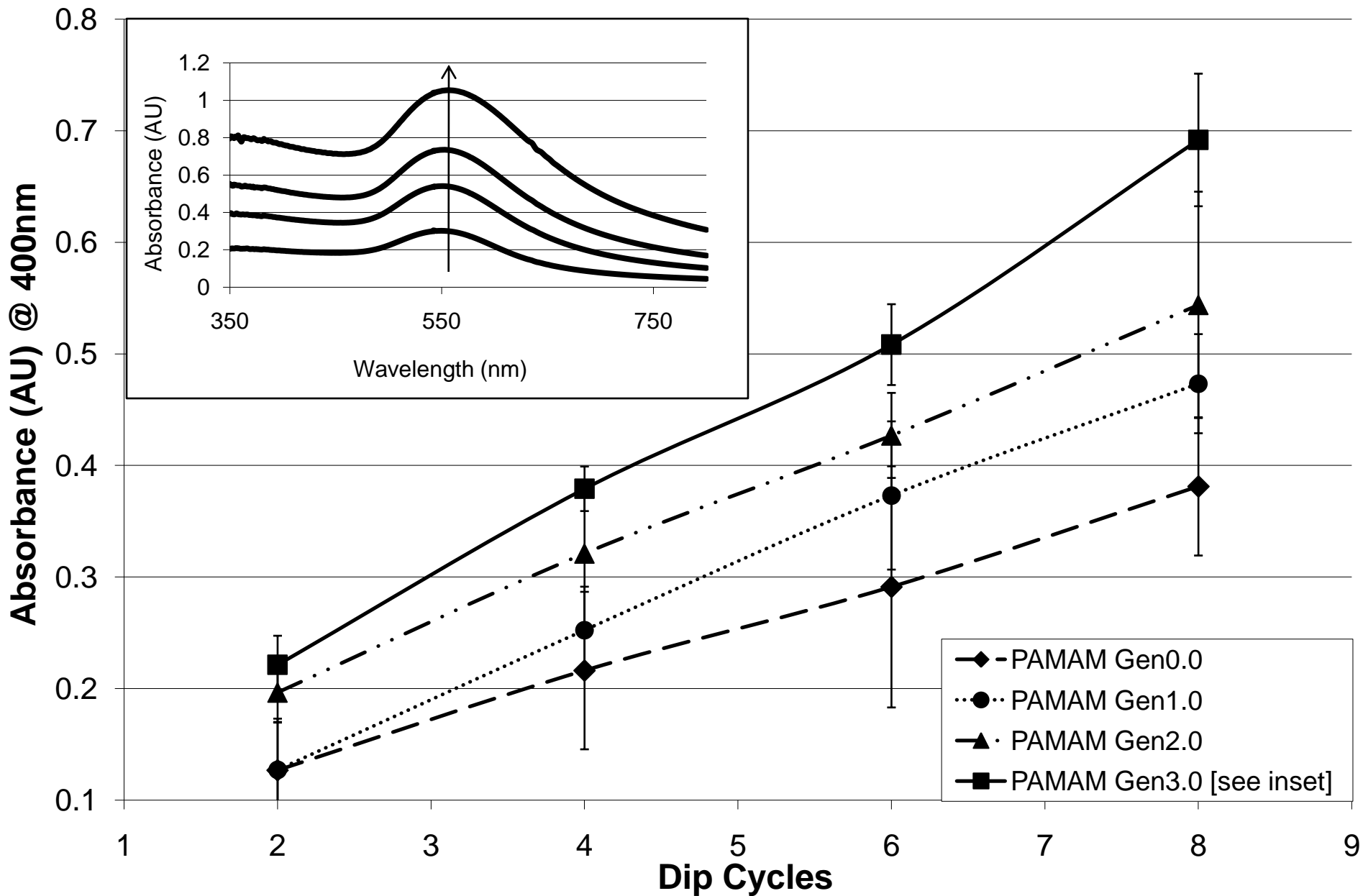
2A: Molecular Weight Growth Comparison of Poly-L-Lysine Linked NP Films



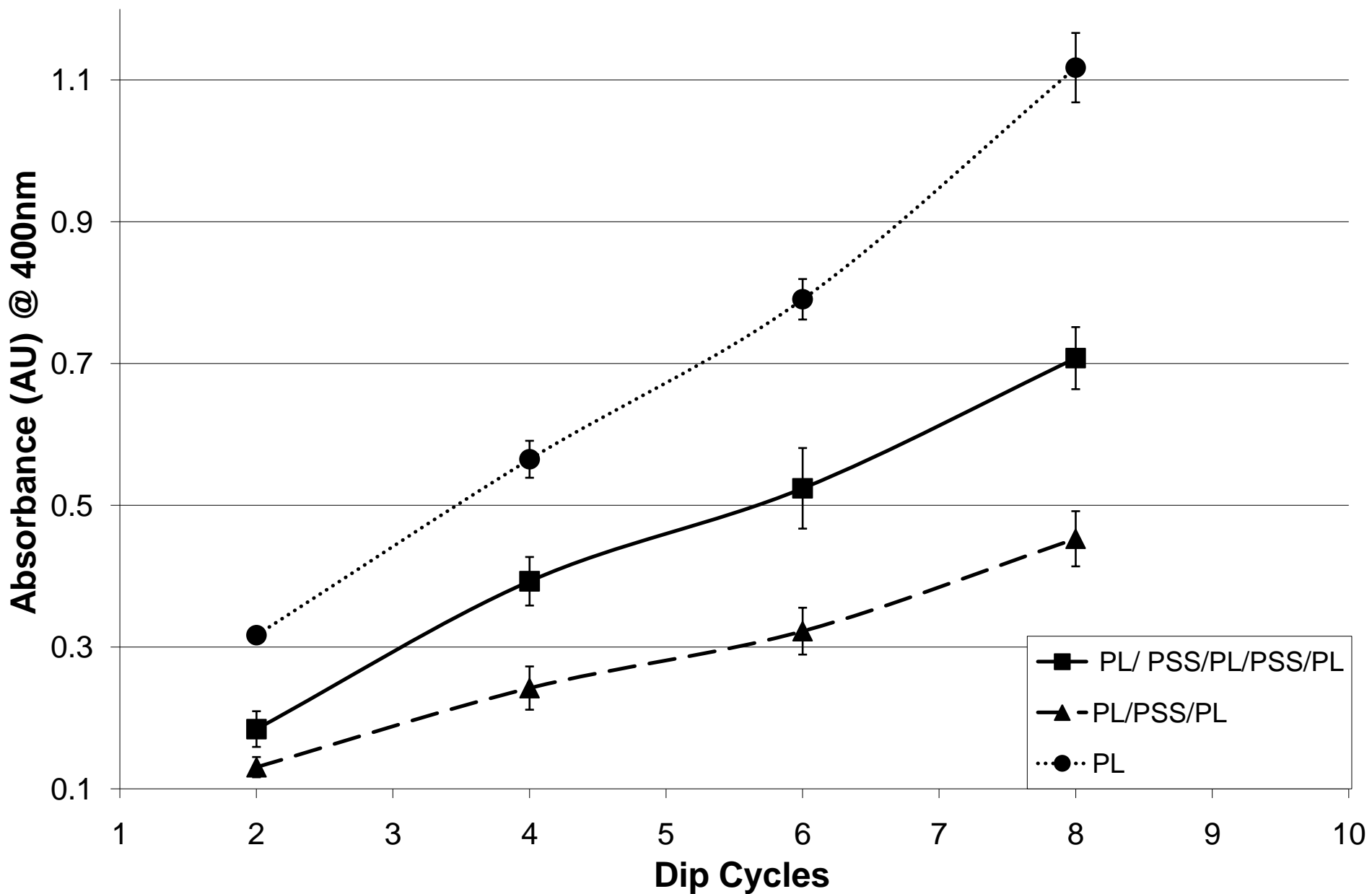
2B: Molecular Weight Growth Comparison of Poly(allylamine) Hydrochloride Linked NP Films



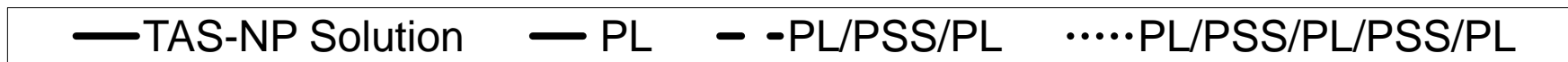
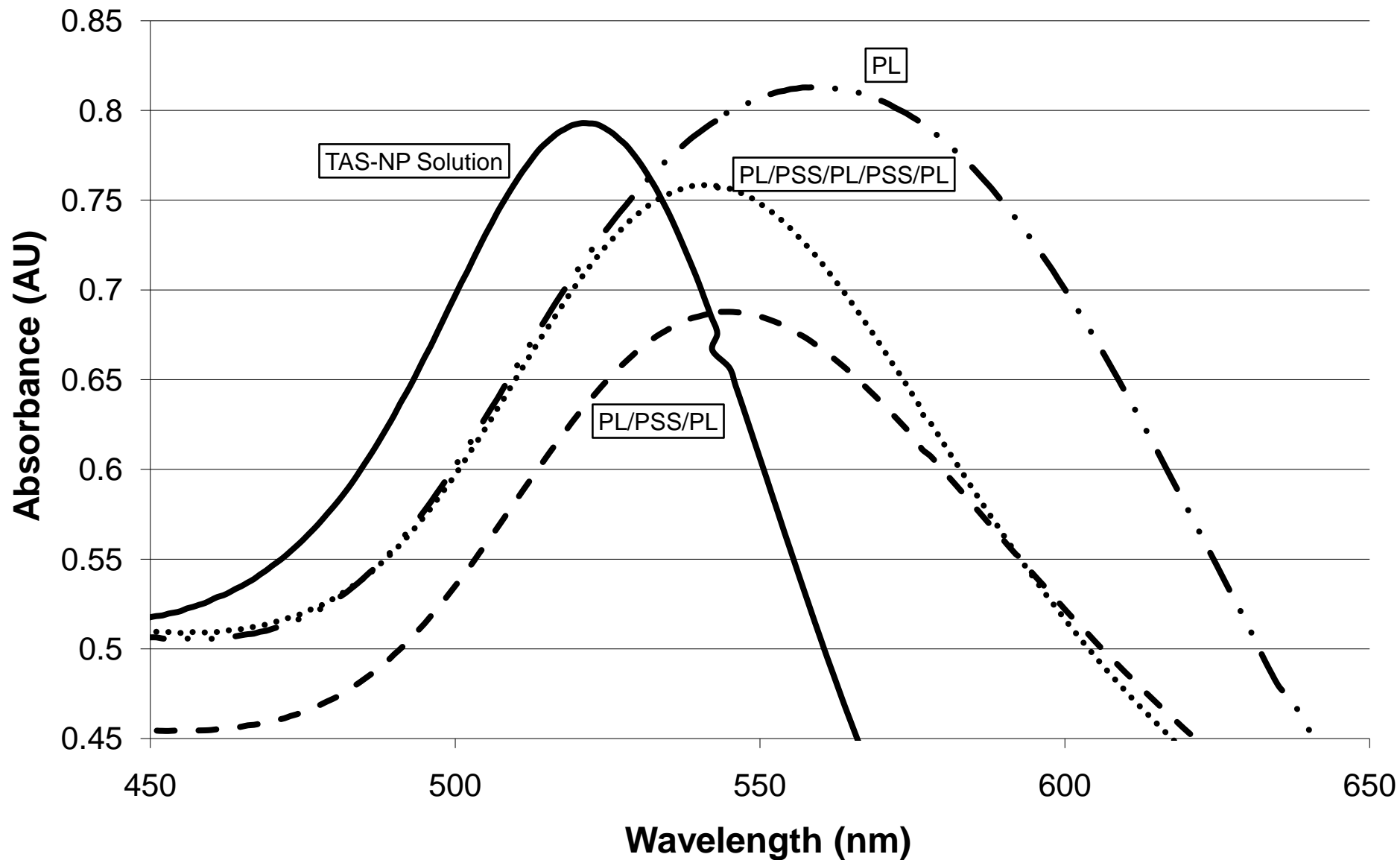
## 2C: Generation Growth Comparison of PAMAM Linked NP Films



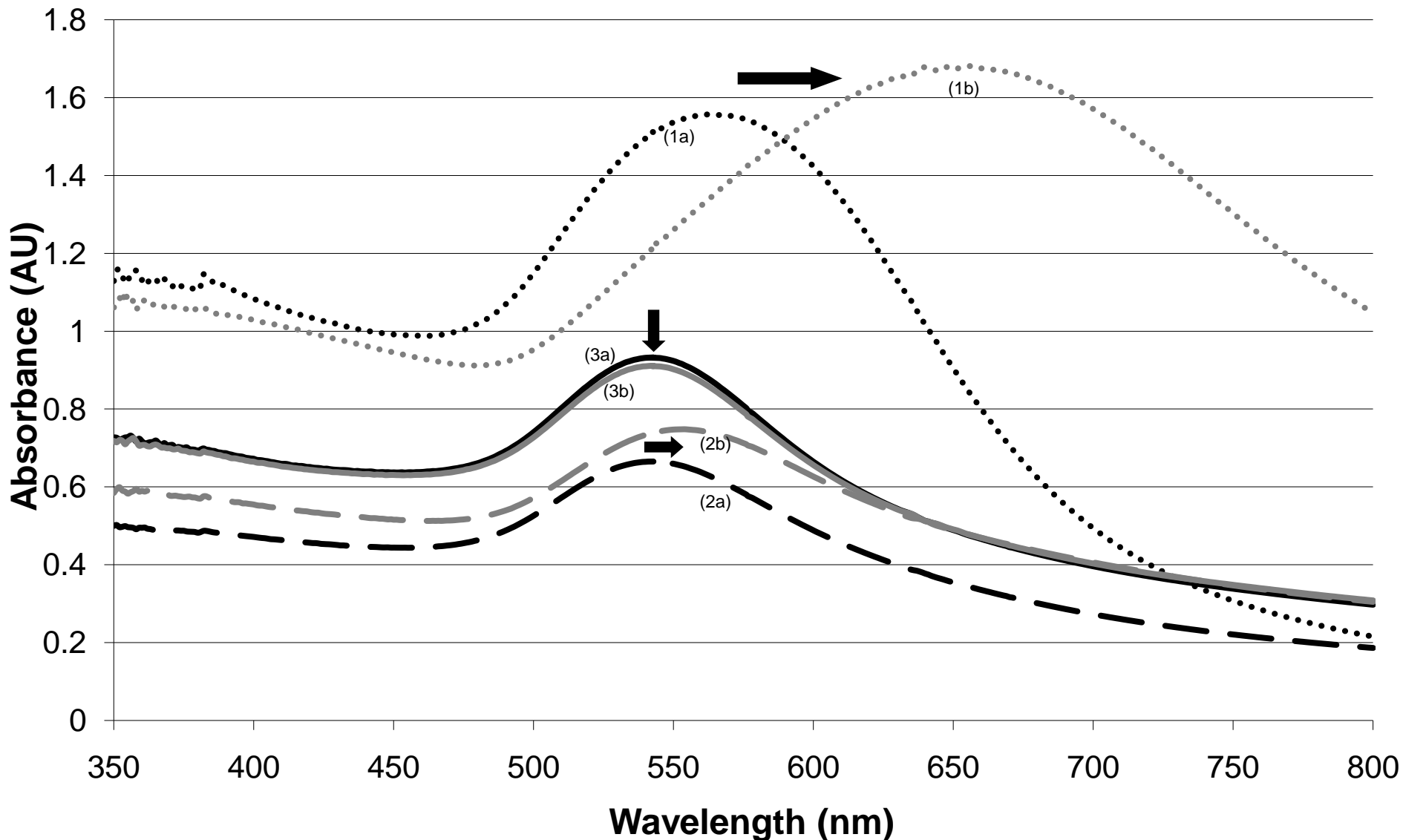
3A: Layered PL/PSS Bridge Film Growth Comparison



3B: Surface Plasmon Band (SPB) Comparison

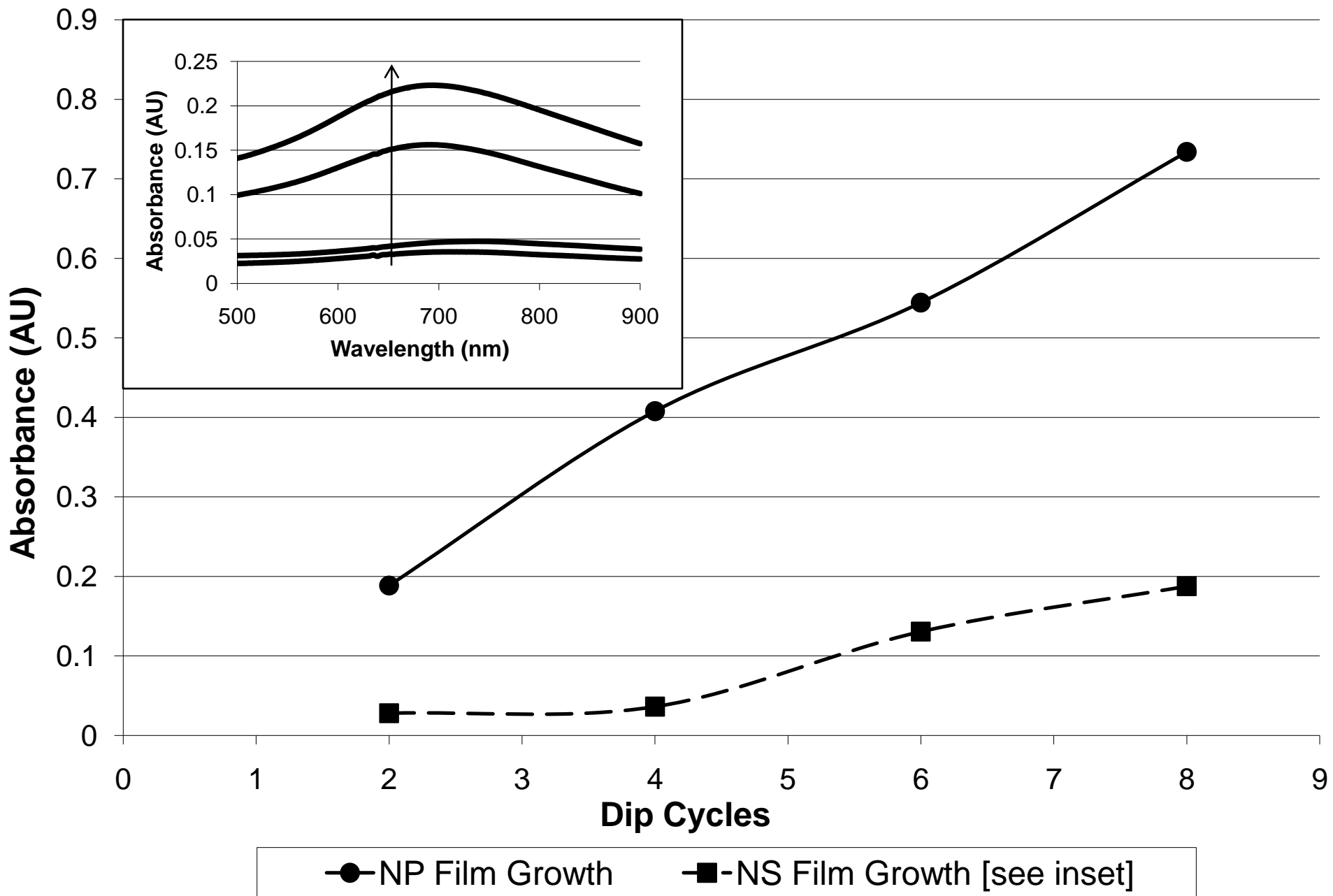


# PL vs. (PL/PSS/PL) vs. (PL/PSS/PL/PSS/PL) Film Stability in Solution and After Air Exposure

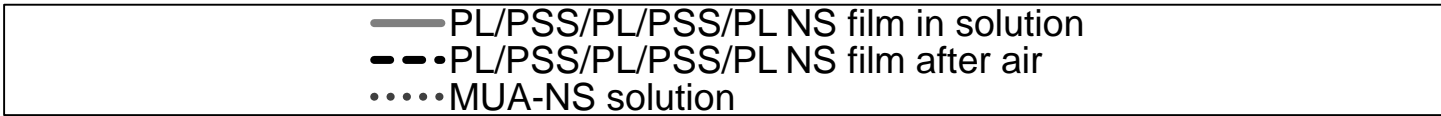
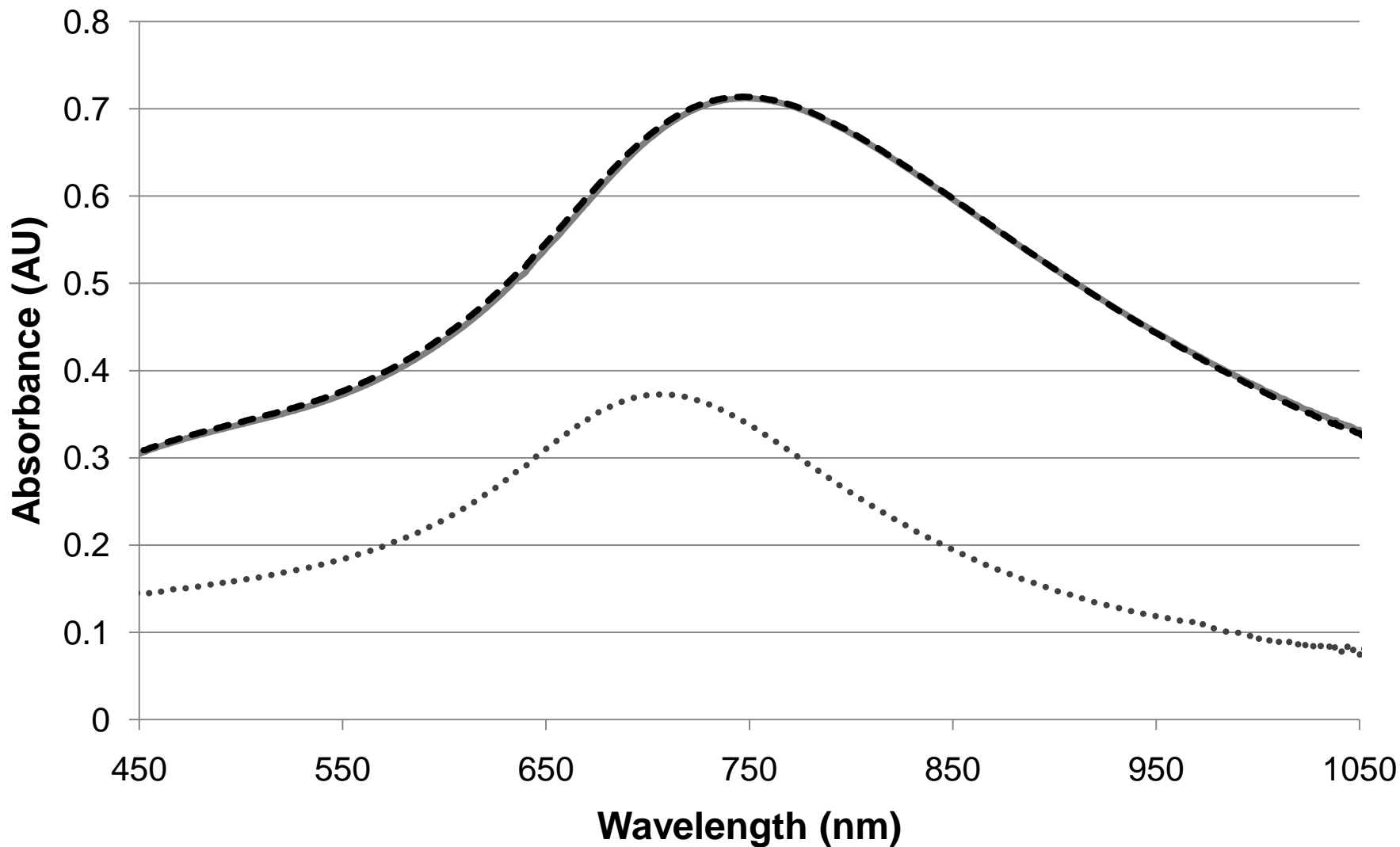


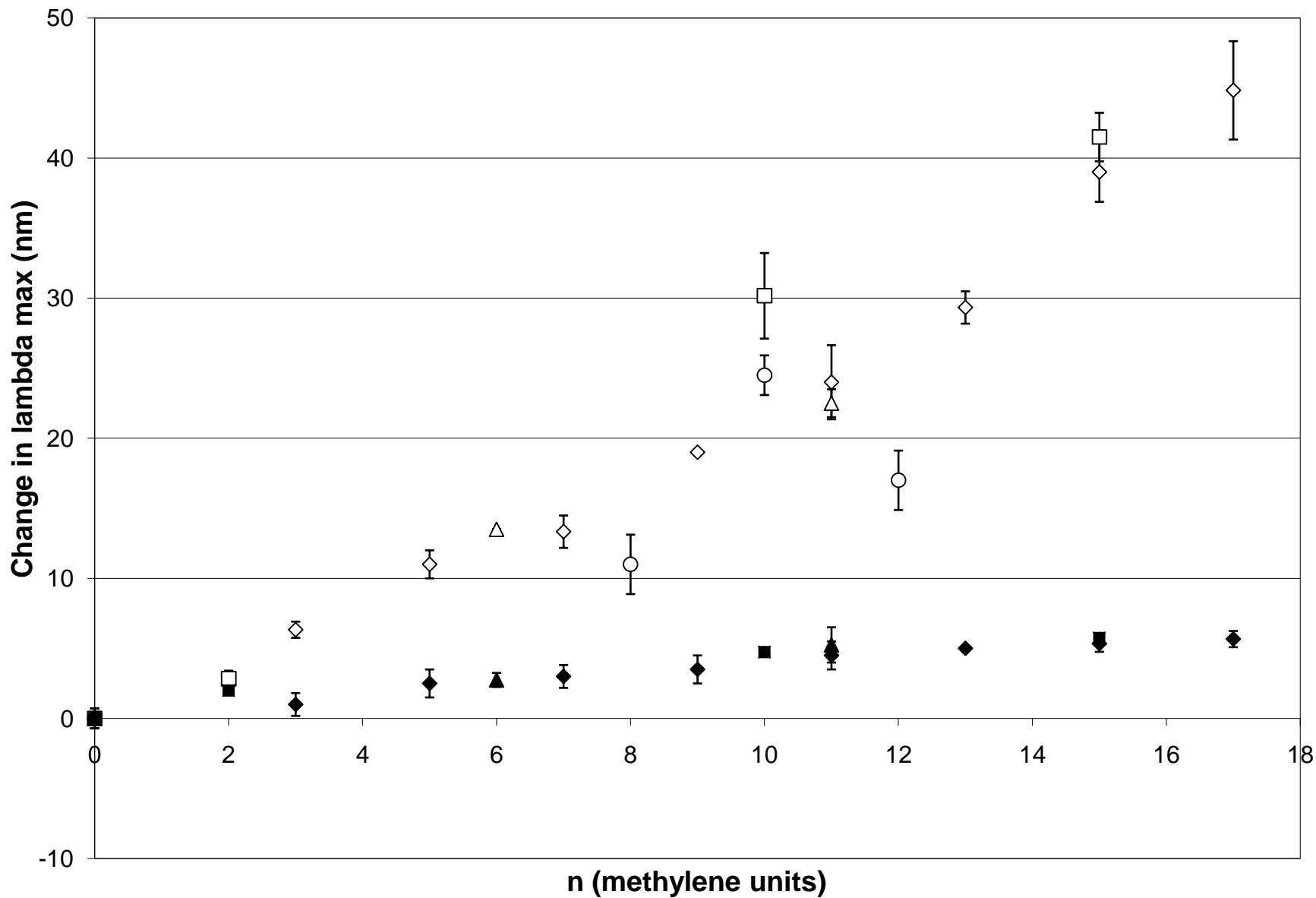


5a. PL/PSS/PL/PSS/PL Film Growth comparison NP(400nm) & NS (600nm)



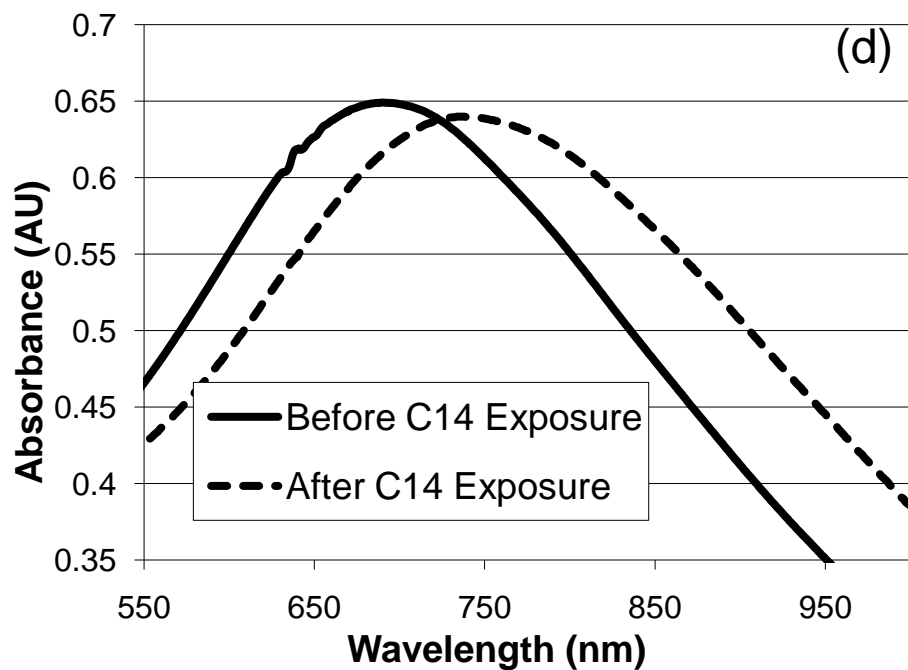
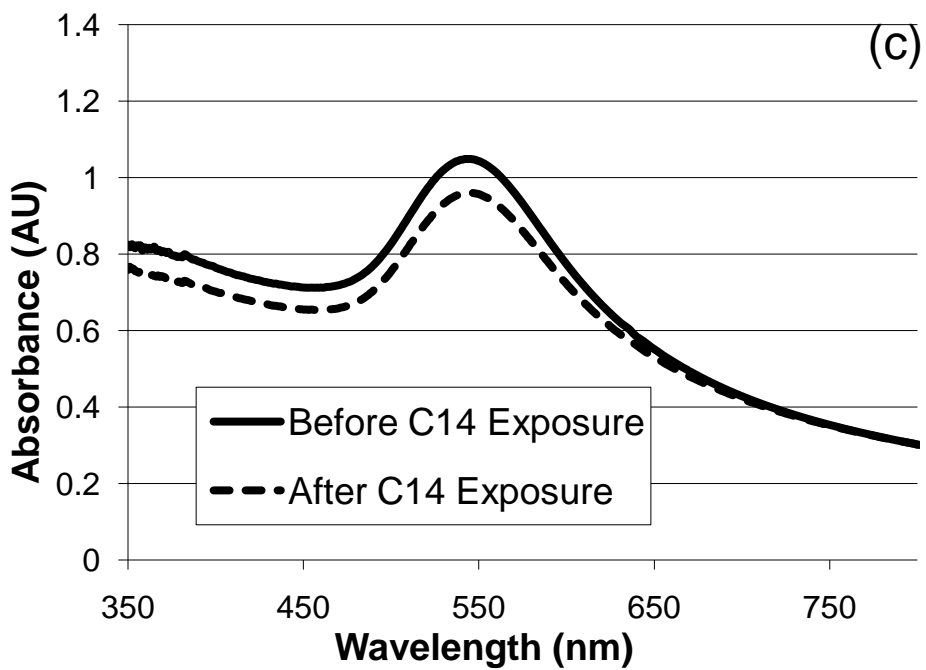
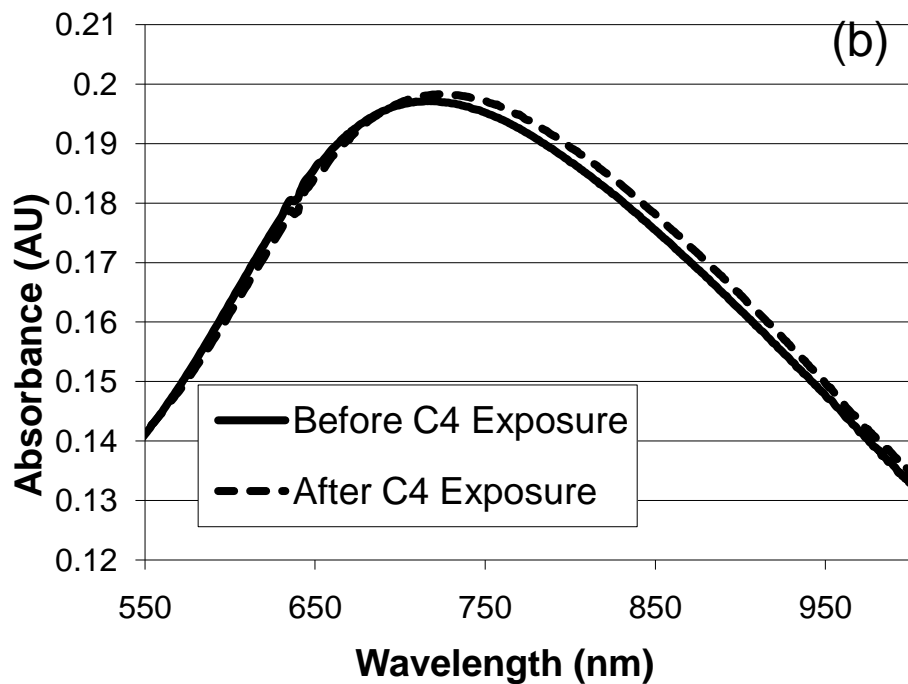
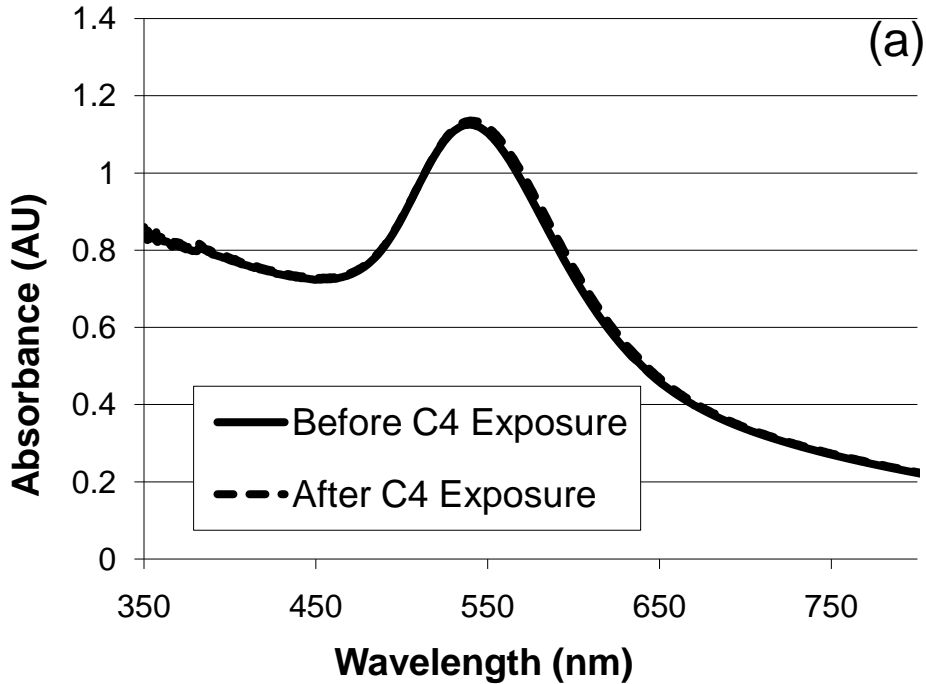
### 5B: Nanoshell films-Before and after air exposure, and MUA-NS solution

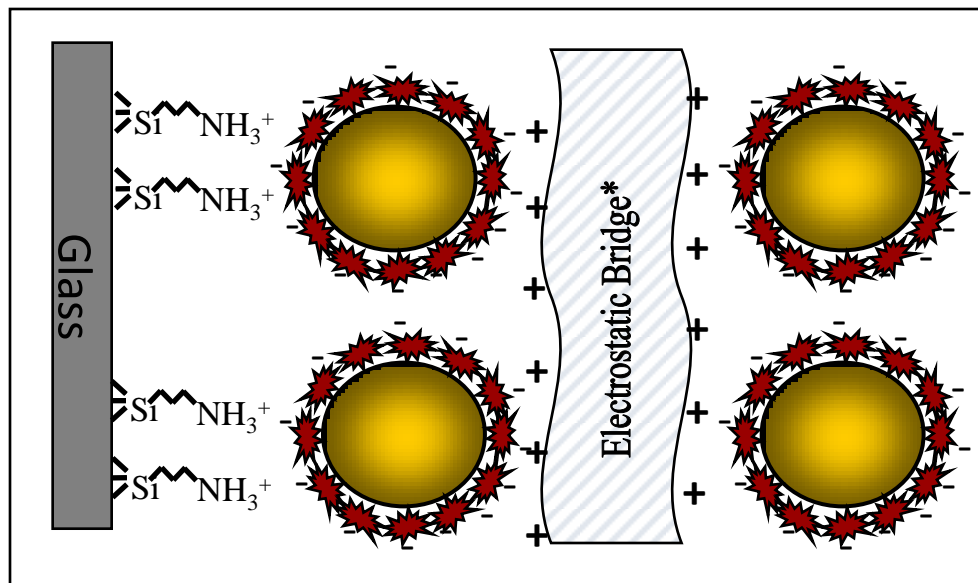




Terminal functional group

- NS-crown ether
- ◇ NS-methyl
- ◆ NP-methyl
- NS-carboxyl
- NP-carboxyl
- △ NS-hydroxy
- ▲ NP-hydroxyl

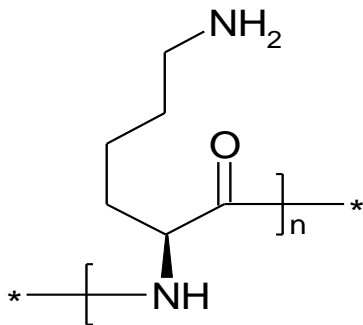




**\* Electrostatic Bridges:**

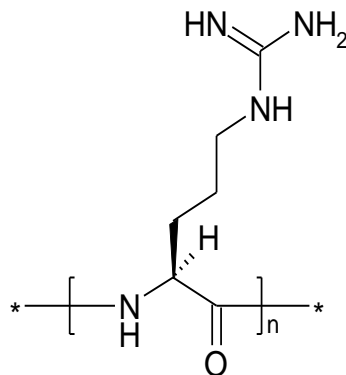
**\*Poly-L-lysine, PL**

$M_w$  15,000-30,000



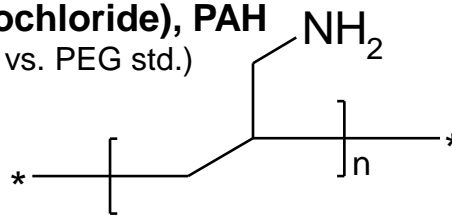
**\*Poly-L-arginine, PA**

$M_w$  15,000-70,000



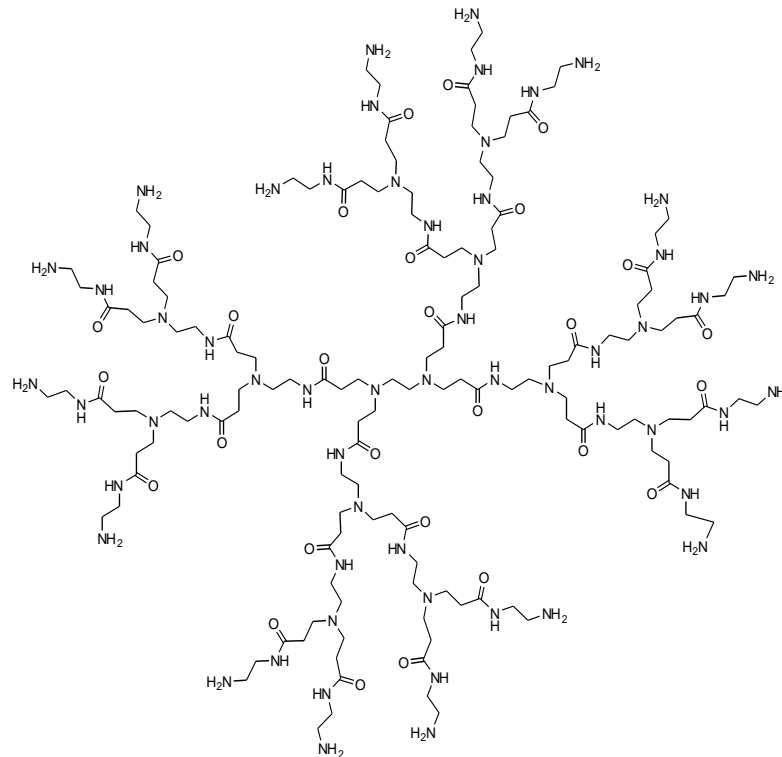
**\*Poly(allylamine hydrochloride), PAH**

average  $M_w$  ~70,000 (GPC vs. PEG std.)



**\*Polyamidoamine Dendrimer**

Gen. 0.0, 1.0, 2.0(pictured), and 3.0



**\*Poly(4-styrenesulfonate), PSS**

average  $M_w$  ~70,000

