

Electronic Supplementary Information for

**Post-infiltration and subsequent photo-cross-linking
strategy to fabricate stable layer-by-layer multilayers
of dendrimers: enabling repeated loading and release
of hydrophobic molecules**

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S1. Film thickness of (PAH/PAMAM)_{7.5} multilayer before and after cross-linking

We have measured the thickness of PAH/PAMAM films before and after cross-linking with sectional view of SEM images. We can observe from the SEM images that the film thickness of PAH/PAMAM decreases from 210 nm before cross-linking (**Fig. S1a**) to 170 nm (**Fig. S1b**) after fully cross-linked. The decreased film thickness suggested that the cross-linked film structure has become more compact than the as-prepared LbL multilayer because the presence of cross-linked junctions has confined the multilayer structure.

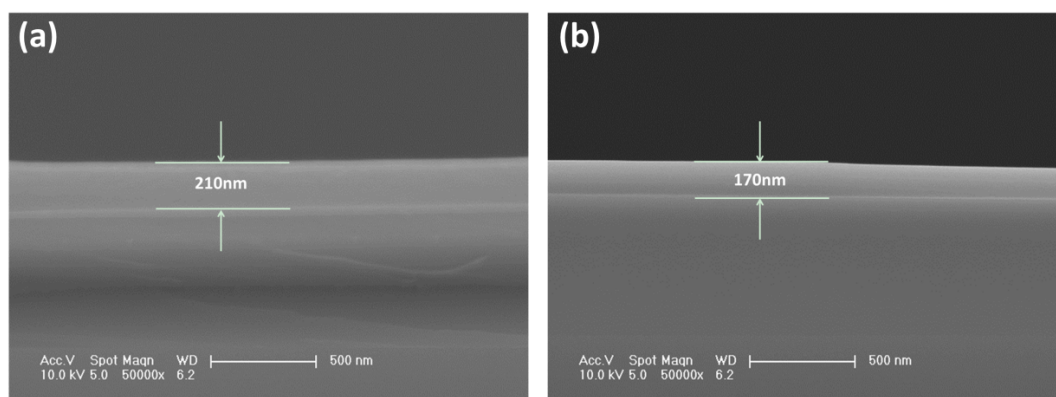


Fig. S1 Sectional view of SEM images of (PAH/PAMAM)_{7.5} multilayer (a) before and (b) after cross-linking.

S2. Film stability in the presence of 75% ethanol

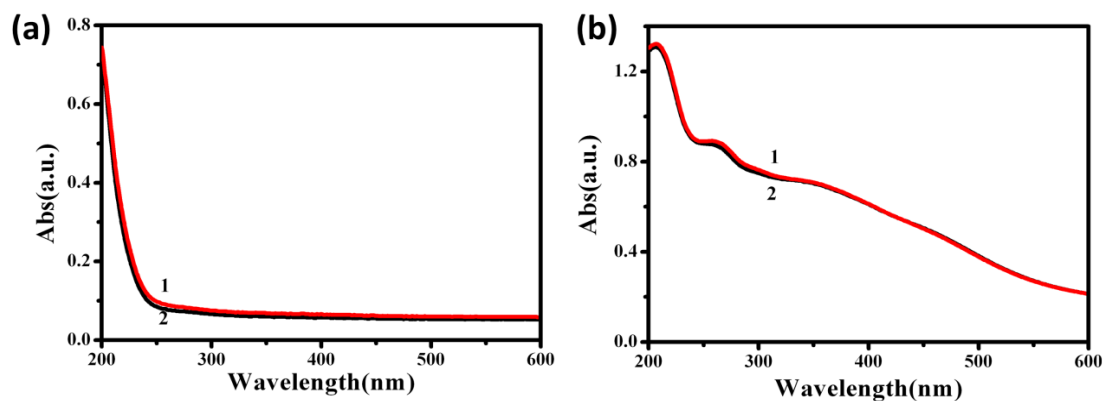


Fig. S2 UV-vis spectra of the (a) uncross-linked multilayers and (b) cross-linked before (red) and after (black) immersion in ethanol solution for 1 h.

S3. The difference of UV-vis curves of absorbed AO between cross-linked and uncross-linked films

Compared with the uncross-linked (PAH/PAMAM)_{7.5} multilayer, the cross-linked (PAH/PAMAM)_{7.5} multilayer has a much higher absorbance thoroughly, as displayed in **Fig. S3a**.

This phenomenon is resulted by the featured absorption of DAS (**Fig. 2** in the text) within the multilayer. Therefore, after loading of AO molecules, the overall absorption of AO for the cross-linked multilayer is completely larger than that of the uncross-linked multilayer. Considering the effect of DAS absorption on the UV-visible spectra, we have compared the UV-visible spectra of AO absorption within the multilayer by the curve after AO absorption minus the curve before AO absorption. Spectra of cross-linked and uncross-linked multilayers were both treated in this way. The results were summarized in (**Fig. S3b**), where Line 1 indicated the uncross-linked multilayer and Line 2 referred to the cross-linked multilayer.

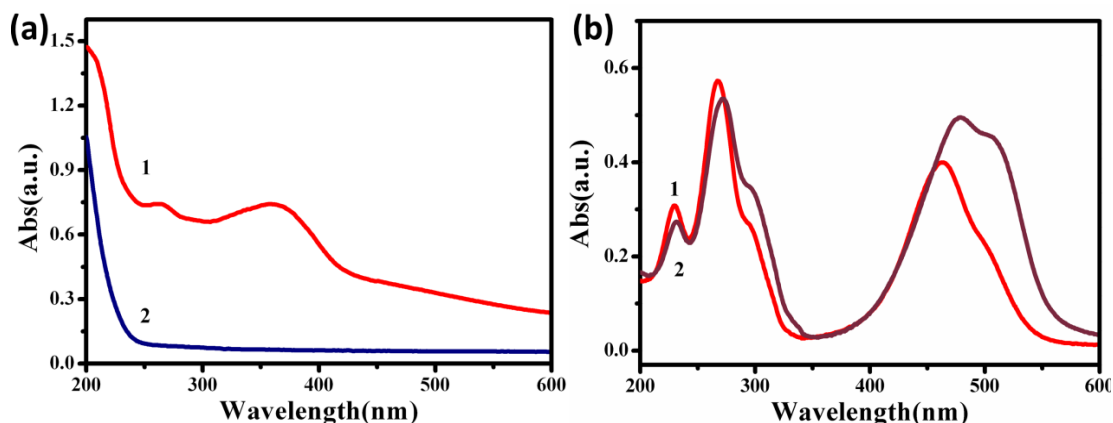


Fig. S3 (a) UV-visible spectra of the as-prepared (1) cross-linked and (2) uncross-linked (PAH/PAMAM)_{7.5} multilayers. (b) The UV-visible curves of the multilayers after fully absorption of AO were plotted after minus the curves before AO absorption. Line 1: uncross-linked (PAH/PAMAM)_{7.5} multilayer; Line 2: cross-linked (PAH/PAMAM)_{7.5} multilayer.

S4. Loaded concentration of AO

Loaded concentration of hydrophobic dye was determined after the dye was totally released to solutions by detecting the concentration of released dye referring to a standard dye curve. To accelerate the releasing behavior, the releasing of AO was carried out in 75% ethanol solution (ethanol/water=3:1 v/v) because the hydrophobic dye has a good solubility in ethanol. The standard curve of AO was obtained in 75% ethanol solution, as displayed in **Fig. S4a**. The uncross-linked and cross-linked (PAH/PAMAM)_{7.5} multilayers after fully loaded with AO molecules were both exposed to 75% ethanol solution for a certain time intervals, followed by stepwise UV-visible spectra characterization of the released AO in 75% ethanol solution in **Fig. S4b**. The released amount of AO was calculated according to the standard curve, which was summarized versus the immersing time in 75% ethanol solution as shown in **Fig. S4c**. For the uncross-linked (PAH/PAMAM)_{7.5} multilayer, the total release was completed at about 5 min and the released amount reached a constant of 50 μg afterwards. For the cross-linked (PAH/PAMAM)_{7.5} multilayer, the releasing process is slow and the complete release took about

60 min to a steady released amount of 47 μg . The slight difference in the loaded AO amount suggested that the highly cross-linked (PAH/PAMAM)_{7.5} multilayer presented a bit lower loading capacity than the uncross-linked film due to the compact structure after cross-linking.

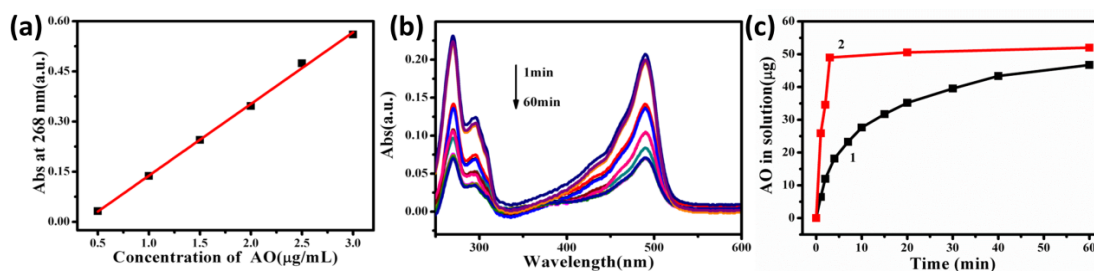


Fig. S4 (a) Standard curve of AO in 75% ethanol solution. (b) Stepwise releasing of AO from cross-linked (PAH/PAMAM)_{7.5} multilayer to 75% ethanol solution. (c) Releasing kinetics of AO in 75% ethanol solution from (1) cross-linked and (2) uncross-linked (PAH/PAMAM)_{7.5} multilayers.

S5. The effects of PAMAM for loading AO

We have investigated film release behaviors versus the film thickness. We have prepared PAH/PAMAM multilayers with 2, 4, 6 bilayers, respectively, which were immersed in an aqueous solution of AO dye molecule (0.2 mg/mL) for 60 min to reach a saturated absorption. The absorbed and released amount was checked through UV-visible spectra as shown in **Fig. S5a-b**. As we can observe from the featured adsorption of AO dye at 268 nm, with the increase of bilayer number (from 2 bilayers to 6 bilayers), the overall absorbance of AO increases, correspondingly. This phenomenon suggested that AO was absorbed within the multilayer instead of simply surface adsorption because the (PAH/PAMAM)₂, (PAH/PAMAM)₄ and (PAH/PAMAM)₆ multilayers have the same PAMAM surface group.

To further confirm the importance of cavity structures within the PAH/PAMAM multilayer contributed from the dendritic PAMAM molecules, we have taken a cross-linked PAH/PAA multilayer without remarkable cavity structures as control and compared absorption behaviors of AO dye molecules between cross-linked PAH/PAA and PAH/PAMAM multilayers. Firstly we fabricated (PAH/PAMAM)_{7.5} and (PAH/PAA)_{7.5}, respectively, which absorbed DAS (aq, 5 mg/mL, pH 3.8) to saturated amount. After fully cross-linked, these two multilayers were immersed in AO aqueous solution (0.2 mg/mL) for 60 min, followed by washing with copious deionized water and drying in nitrogen flow. The loaded AO amount was checked by UV-visible spectra as shown in **Fig. S5c**. As we can observe from the featured absorption of AO at 268 nm, the AO amount loaded within PAH/PAMAM multilayer is much larger (almost 3.2 times) than that within PAH/PAA. This result indicates that under identical number of bilayer, the PAH/PAMAM multilayer has a higher loading capacity than PAH/PAA, which is attributed to the

cavity structure formed by the highly branched PAMAM molecules. Therefore, the increasing dye amount dependent on the number of PAH/PAMAM bilayer in **Fig. S5a-b** could also be well interpreted by the growing cavity structures for increasing loading capacity of dye molecules.

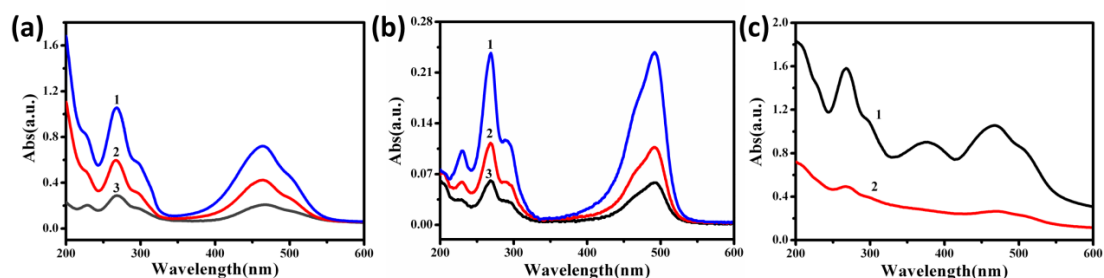


Fig. S5 (a) UV-visible spectra of AO absorbed within (1) (PAH/PAMAM)₆, (2) (PAH/PAMAM)₄ and (3) (PAH/PAMAM)₂ multilayers on quartz substrate. (b) UV-visible spectra of AO releasing amount of (1) (PAH/PAMAM)₆, (2) (PAH/PAMAM)₄ and (3) (PAH/PAMAM)₂ multilayers in aqueous solution. (c) UV-visible spectra of cross-linked (1) (PAH/PAMAM)_{7.5} and (2) (PAH/PAA)_{7.5} after immersed in AO aqueous solution for 60 min.

S6. The relaxation of the internal structure of the multilayers

To clarify the stability of the film structure in the loading-releasing of AO in ethanol, we have checked durability of the uncross-linked (PAH/PAMAM)_{7.5} multilayer in the presence of ethanol. The as-prepared (PAH/PAMAM)_{7.5} multilayer was exposed to 75% ethanol solution for 90 min before loading of AO molecules. Afterwards, the multilayer was immersed in AO aqueous solution for 1 h, followed by rinsing with water, drying with nitrogen and characterized with UV-visible spectra in **Fig. S6a** (Line 2). Control experiment was carried out by immersing the as-prepared (PAH/PAMAM)_{7.5} multilayer in AO aqueous solution for 1 h, followed by identically rinsing and drying (Line 1 in **Fig. S6a**). The results showed that by pre-treating the multilayer with ethanol solution, its loading capacity of AO decreased dramatically, indicating that the treatment of ethanol might reduce the loading capacity of the multilayer to some degree. Therefore, in the cycled loading-releasing experiments, the relaxation of the film structure with the number of cycles performed may be caused by the decreased loading capacity.

Moreover, the stability of uncross-linked films in presence of the hydrophobic dye has been checked. We immersed the (PAH/PAMAM)_{7.5} multilayer in aqueous solution of AO (0.2 mg/mL)

for 60 min to load the AO molecules. The stability of the (PAH/PAMAM)_{7.5} multilayer loaded with AO was checked by treatment of alkaline solution (NaOH) with a pH value of 12 for 30 min. As we can observe from **Fig. S6b**, featured absorption of the (PAH/PAMAM)_{7.5} multilayer in the presence of AO totally disappeared, indicating that the film is not stable in alkaline.

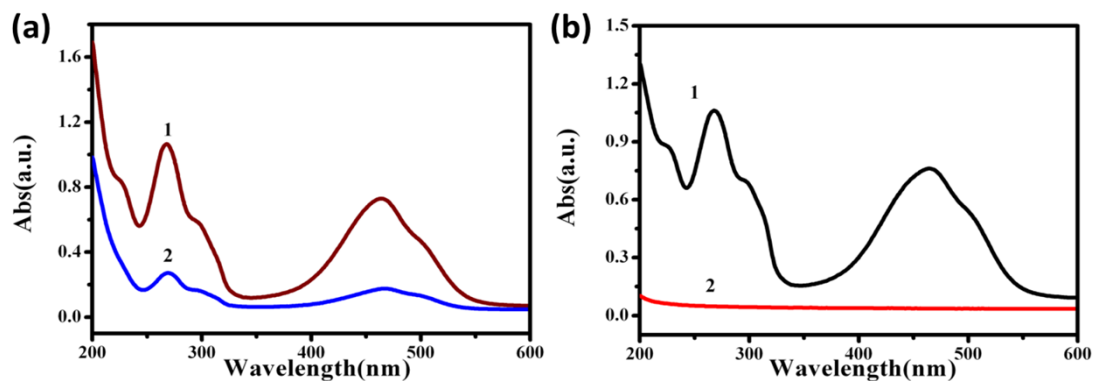


Fig. S6 (a) UV-visible spectra of (PAH/PAMAM)_{7.5} multilayer after absorbing AO (1) without or (2) with pre-treatment of ethanol solution. (b) UV-visible spectra of (PAH/PAMAM)_{7.5} multilayer (1) loaded with AO and (2) after immersed in alkaline solution for 30 min.