

# PAH/DAS covalently cross-linked Layer-by-Layer multilayers: a “nano-net” superstratum immobilizes nanoparticles and remains permeable to small molecules

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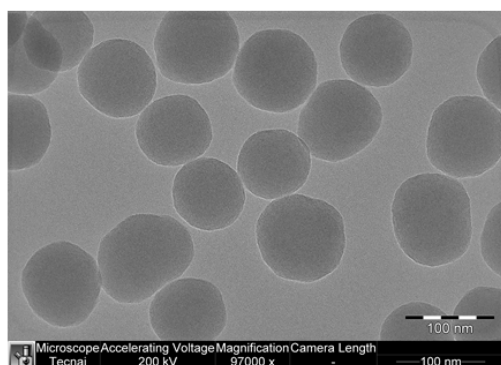


Figure S 1. TEM images of synthesized silica nanoparticles.

**Table S1.** Residual ratio of the multilayered films after treatment in basic solutions (pH 14) for different period of time. \*Uncross-linked: (SiO<sub>2</sub> NP/PAH)<sub>5</sub> films. \*\*Cross-linked: (SiO<sub>2</sub> NP/PAH)<sub>5</sub> films post-infiltrated by DAS followed by cross-linking.

	Immersion for 30min	Immersion for 4h
Uncross-linked*	93.7%	61.1%
Cross-linked**	80.7%	46.3%

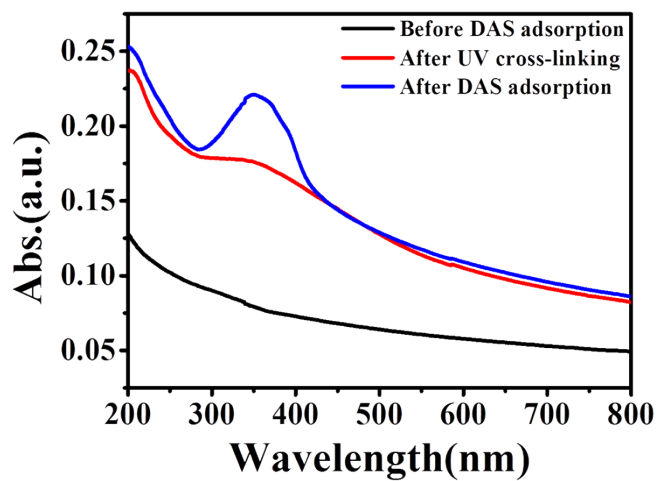


Figure S 2. UV-vis spectra for the  $(\text{PAH}/\text{SiO}_2\text{NP})_5$  multilayers (black), and the films after infiltrated by DAS (red), and after UV light-induced decomposition of DAS.

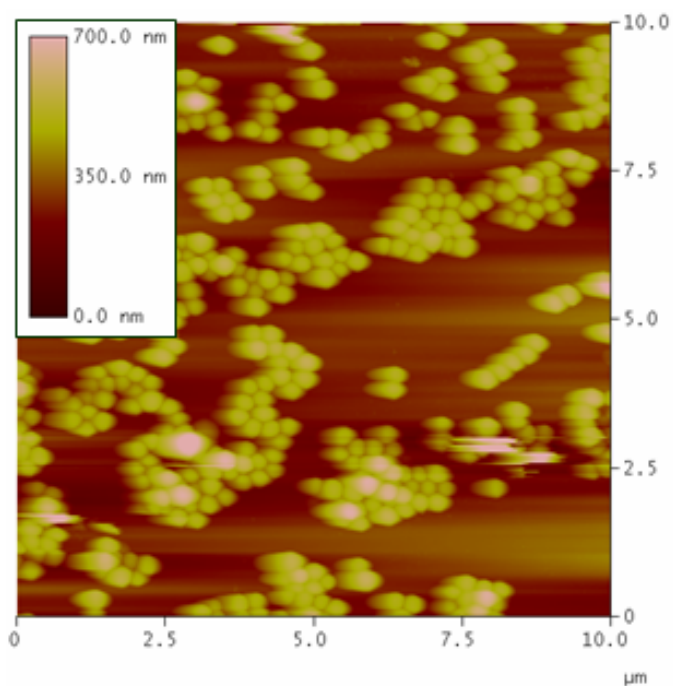


Figure S 3. AFM image of the surface morphology of  $(\text{PAH}/\text{SiO}_2\text{NP})_5$  multilayers.

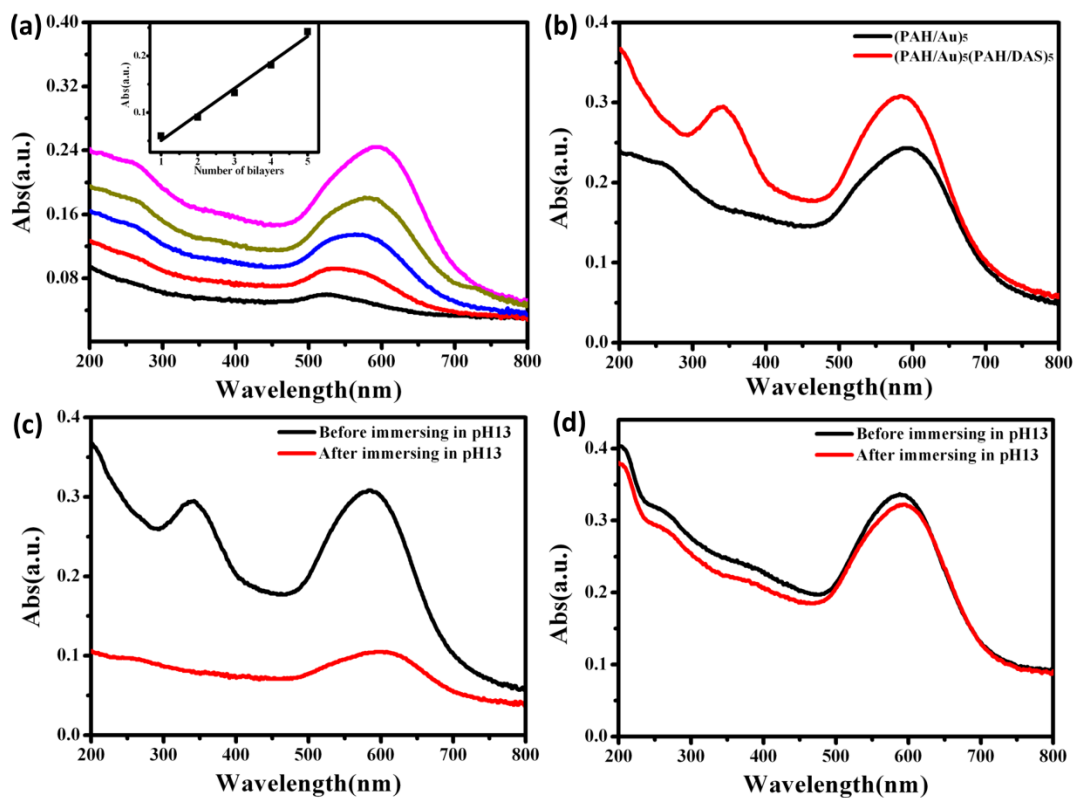


Figure S 4. (a) UV-vis spectra following the assembly process of the  $(\text{PAH}/\text{Au})_5$  LbL films. The inset indicates linear relationship between the absorbance of the film and the number of bilayers. (b) UV-vis spectra of the  $(\text{PAH}/\text{Au})_5$  LbL films (black) and the  $(\text{PAH}/\text{Au})_5(\text{PAH}/\text{DAS})_5$  LbL films (red). (c) UV-vis spectra of the UNCROSS-LINKED  $(\text{PAH}/\text{Au})_5(\text{PAH}/\text{DAS})_5$  LbL film before (black) and after (red) immersion in the basic solution. (d) UV-vis spectra of the CROSS-LINKED  $(\text{PAH}/\text{Au})_5(\text{PAH}/\text{DAS})_5$  LbL film before (black) and after (red) immersion in the basic solution.

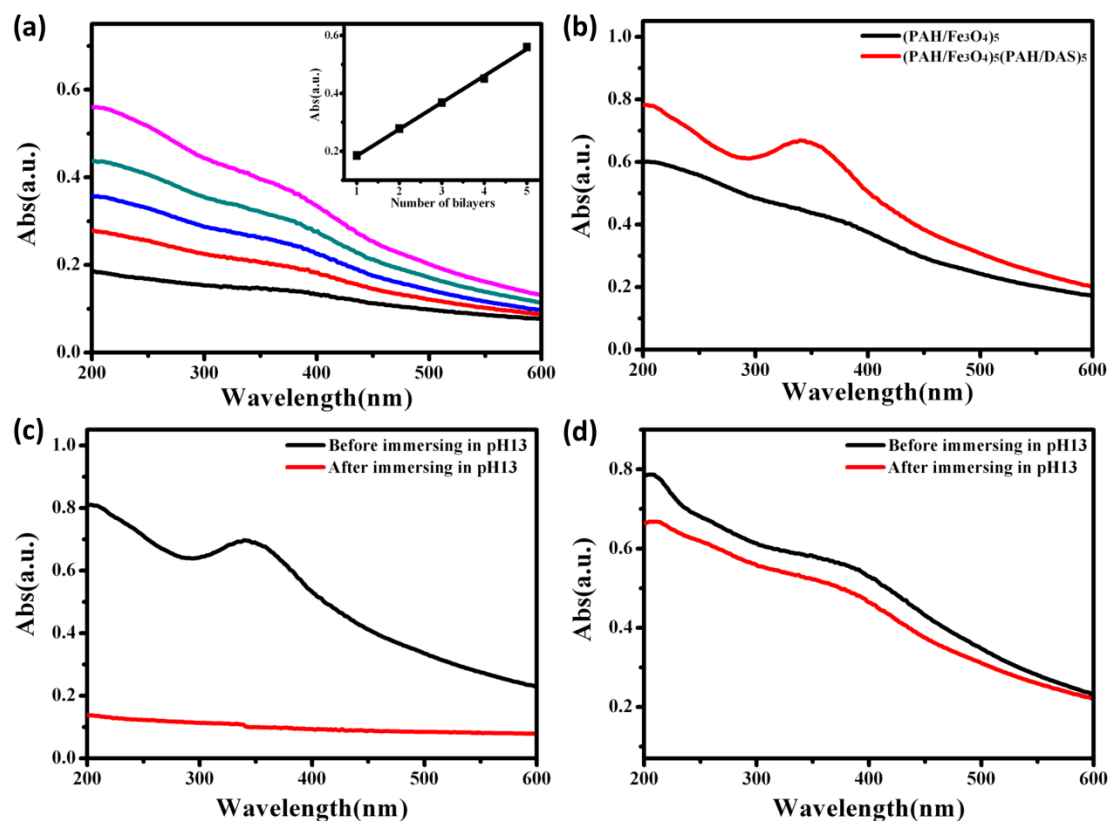


Figure S 5. (a) UV-vis spectra following the assembly process of the (PAH/Fe<sub>3</sub>O<sub>4</sub>)<sub>5</sub> LbL films. The inset indicates linear relationship between the absorbance of the film and the number of bilayers. (b) UV-vis spectra of the (PAH/Fe<sub>3</sub>O<sub>4</sub>)<sub>5</sub> LbL films (black) and the (PAH/Fe<sub>3</sub>O<sub>4</sub>)<sub>5</sub>(PAH/DAS)<sub>5</sub> LbL films (red). (c) UV-vis spectra of the UNLINKED (PAH/Fe<sub>3</sub>O<sub>4</sub>)<sub>5</sub>(PAH/DAS)<sub>5</sub> LbL film before (black) and after (red) immersion in the basic solution. (d) UV-vis spectra of the LINKED (PAH/Fe<sub>3</sub>O<sub>4</sub>)<sub>5</sub>(PAH/DAS)<sub>5</sub> LbL film before (black) and after (red) immersion in the basic solution.

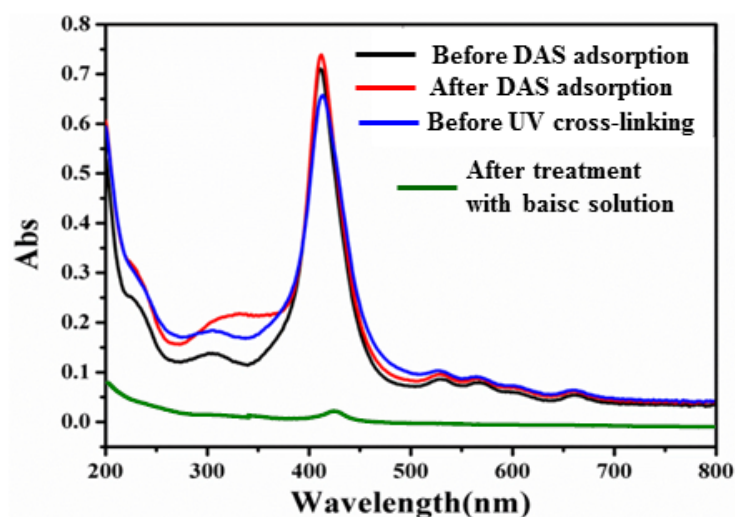


Figure S 6. UV-vis spectra for the (PAH/Por)<sub>5</sub> multilayers (black), and the films after infiltrated by DAS (red), and after UV light-induced decomposition of DAS, and after treatment using the basic solution (green).

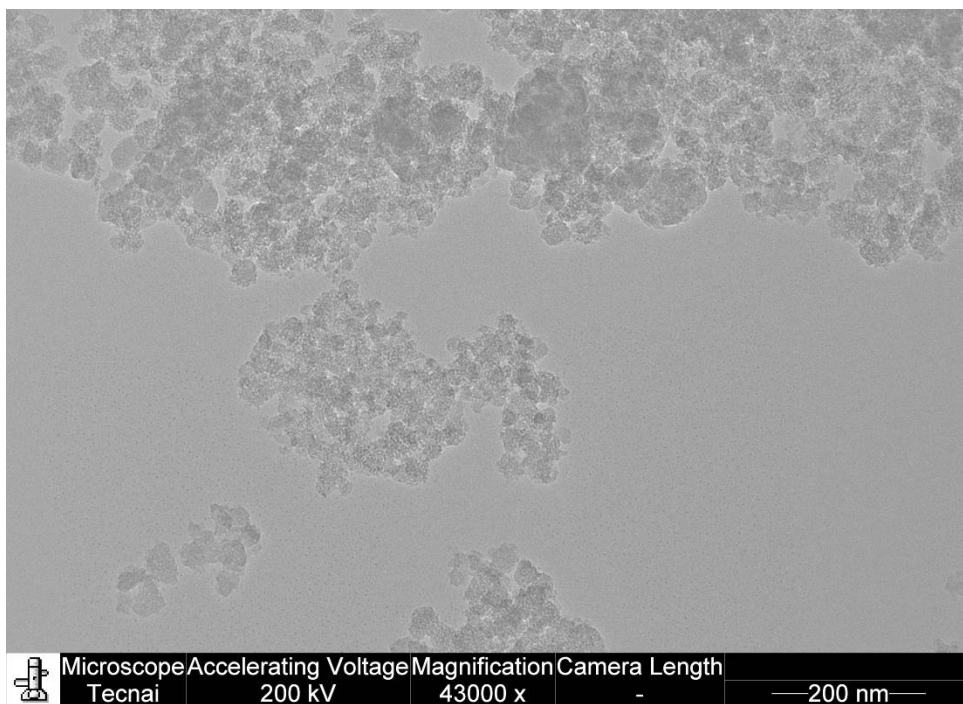


Figure S 7. TEM images of the prepared mesoporous silica nanoparticles.

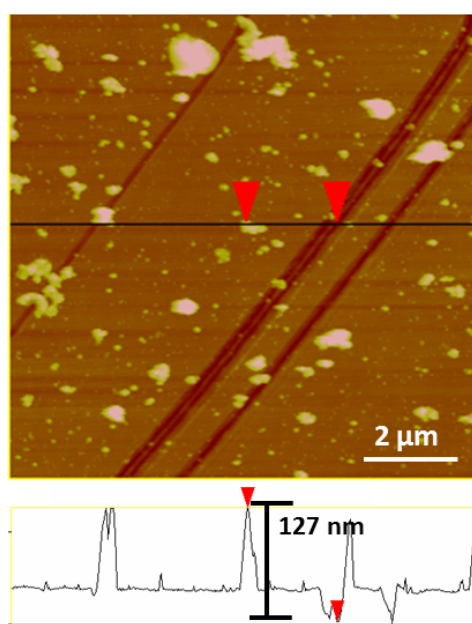


Figure S8. AFM image of the surface morphologies of cross-linked  $(\text{MP SiO}_2 \text{ NP/PAH})_5(\text{PAH/DAS})_5$  multilayers.

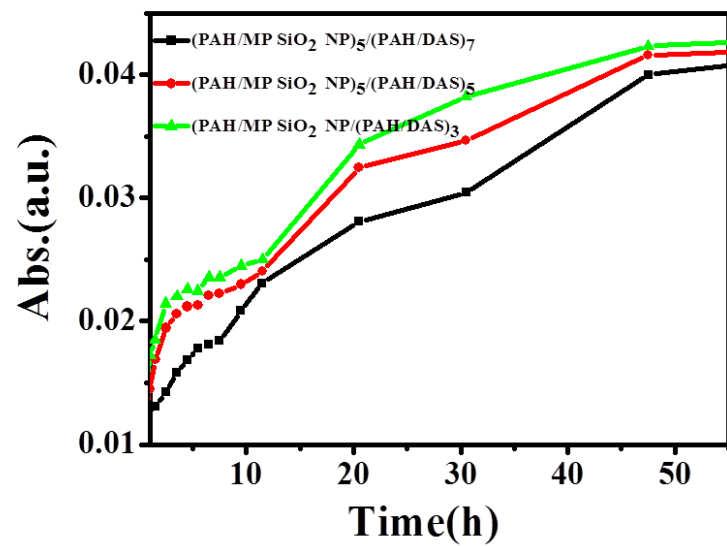


Figure S 9. Release profile of MB from (MP SiO<sub>2</sub> NP/PAH)<sub>5</sub>(PAH/DAS)<sub>n</sub> (n=3,5,7).