Supporting Information

Notable Third-Order Optical Nonlinearities realized in Layer-by-Layer Assembled Composite Films by Intercalation of Porphyrin/Polyoxometalate into Layered Double Hydroxide

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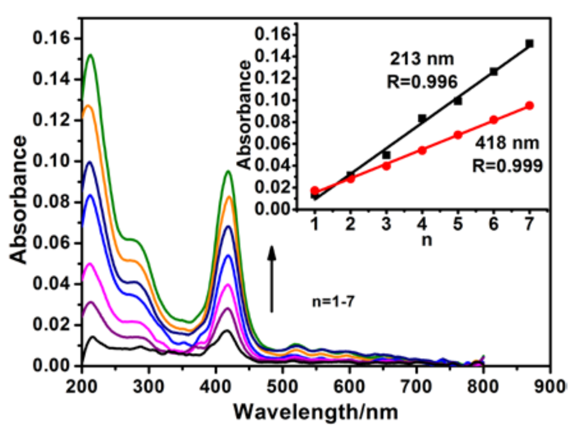

Figure S1. UV-vis absorption spectra of (LDH/P_5W_{30})$_n$/LDH (n = 1 - 7) films, The insert shows the plot of the absorbance versus number of bilayers at 213 nm

Figure S1 shows the UV-vis absorption spectra of (LDH/P_5W_{30})$_n$/LDH (n=1-7) fims with different bilayers. They exhibit the characteristic absorption band in 213 nm and 278 nm, corresponding to O→W charge transition in POM.[1] It indicates that the films contain P_5W_{30} anions. The absorbance of films in 213 nm increases linearly with the increase of bilayer number, demonstrating a uniform growth and the same content of POM each bilayer.

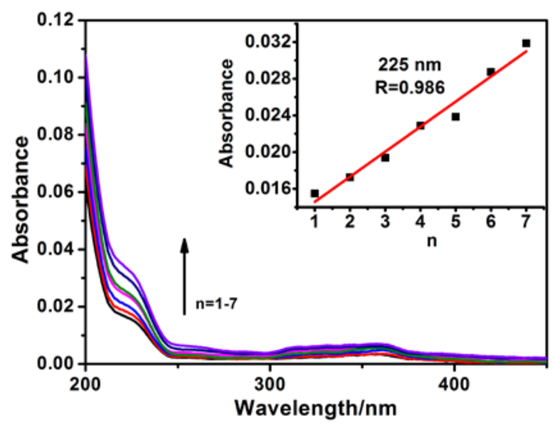

Figure S2. UV-vis absorption spectra of PAH/PSS/(LDH/PSS)$_n$/LDH (n = 1 - 7) films. The insert shows the plot of the absorbance at 225 nm versus number of layers.

The PAH/PSS/(LDH/PSS)$_n$/LDH (n = 1 - 7) films exhibit an absorption band around 225 nm (Figure S2), which is characteristic absorption band of PSS. The absorbance of this band increases with the increase of the number of bilayers. It demonstrates that the PSS/LDH films grew uniformly on the subatrate, and PAH, PSS and LDH were assembled into the PAH/PSS/(LDH/PSS)$_n$/LDH films successfully.

Z-scan equipment. Z-scan is one of the ordinary methods for the determination of third-order nonlinear optical property. It has simple apparatus and high sensitivity. The sign and value of nonlinear absorption and nonlinear refraction can be obtained directly in this method. In this article, we use Z-scan method to determine the third-order nonlinear optical property.

In the Z-scan test, a Gaussian laser beam was used. The laser beam transmitting through attenuator was divided into two beams. The reference beam was detected directly to minimize the error. The other beam focused transmitted through the sample and was detected by another detector. The sample was fixed on the precision step motor and moved around the focus. The light intensity on the sample was changed gradually. The signal received by detectors was inputted into computer, Z-scan curves were obtained after the processing.

Computing method of Z-scan. The data processing of Z-scan experiment was done according to reference.[2] The details were as follows.

When only the third-order nonlinear optical property is considered among all of the nonlinearities, the refraction of sample can be expressed though

$$n=n_0+\frac{1}{2}n_2|E|^2=n_0+\gamma I \quad (1)$$

Where n_0 is linear refraction; n_2 and γ is nonlinear refraction with different unit; E is amplitude of incident laser; I is the irradiance of incident laser. n_2 and γ are related through the formula:

$$n_2(esu)=\frac{cn_0}{40\pi}\gamma(m^2/W) \quad (2)$$

Where c is the vacuum speed of light.

If the sample is thin enough, $L \ll Z_0$, L is the thickness of sample, Z_0 is the diffraction length of laser.

If we take no account of nonlinear absorption, when the laser beam transmits through sample and the aperture, the normalized transmittance is

$$T(z)=\frac{\int_{-\infty}^{\infty} P_T[z,\Delta\Phi_0(t)]dt}{S\int_{-\infty}^{\infty} P_I(t)dt} \tag{3}$$

Where

$$\Delta\Phi_0(t)=k\gamma I_0(t)L_{eff} \tag{4}$$

$$L_{eff}=\frac{1-e^{-\alpha_0 L}}{\alpha_0} \tag{5}$$

$$P_I(t)=\frac{1}{2}\pi\omega_0^2 I_0(t) \tag{6}$$

$P_T[z,\Delta\Phi_0(t)]$ is the optical power of beam transmitting though the aperture, $\Delta\Phi_0(t)$ is the phase change at the focus, $k=2\pi/\lambda$， λ is wavelength, $I_0(t)$ is light intensity at the aperture, L_{eff} is the effective thickness of sample, α_0 is the linear absorption coefficient of sample, $P_I(t)$ is the optical power of incident laser beam, ω_0 is waist radius， S is the transmittance of the aperture.

Theoretical calculation shows that if the difference of the peak and valley is defined as

$\Delta T_{P\text{-}V}=T_P-T_V$, when $|\Delta\Phi 0|\leq\pi$

$$\Delta T_{P\text{-}V}=0.406(1\text{-}S)^{0.25}|\Delta\Phi_0| \tag{7}$$

Therefore, the third-order nonlinear refractive index can be calculated according to the formulas (4), (5), (6) and (7).

When the nonlinear absorption is considered, the absorption coefficient of sample can be expressed as follows.

$$\alpha=\alpha_0+\beta I \qquad (8)$$

α_0 is the linear absorption coefficient, β is the nonlinear absorption coefficient.

β with different units can be related through the formula:

$$\beta(esu)=\frac{cn_0\beta(m/w)}{8000\,\pi} \qquad (9)$$

We define

$$q_0(z,t)=\frac{\beta I_0(t)L_{eff}}{1+\frac{z^2}{z_0^2}} \qquad (10)$$

When $|q_0|<1$, the normalized transmittance is

$$T(z,S=1)=\sum_{m=0}^{\infty}\frac{[-q_0(z,0)]^m}{(m+1)^{\frac{3}{2}}} \qquad (11)$$

Based on the above formula, the nonlinear nonlinear absorption coefficient can be calculated.

The third-order nonlinear optical polarizability can be obtained according to the formulas bellow with the nonlinear absorption coefficients and nonlinear refractive index.

$$Re\chi^{(3)}(esu)=\frac{cn_0^2}{120\pi^2}\gamma(m^2/W) \qquad (12)$$

$$Im\chi^{(3)}(esu)=\frac{c^2n_0^2}{240\pi^2\omega}\beta(m/W) \qquad (13)$$

$$\chi^{(3)}(esu)=\sqrt{[Re\chi^{(3)}(esu)]^2+[Im\chi^{(3)}(esu)]^2} \qquad (14)$$

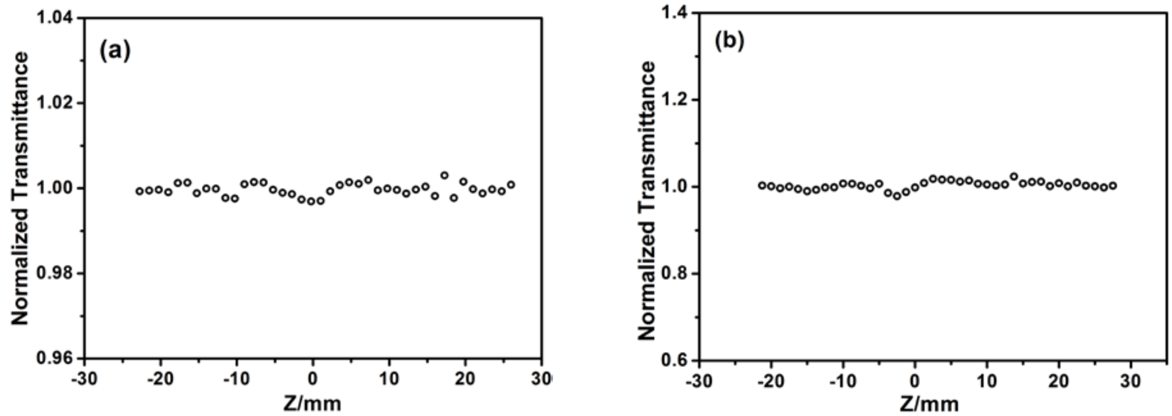

Figure S3. Open aperture curve (a) and Closed aperture curve (b) for PAH/PSS/(LDH/PSS)$_{20}$/LDH film.

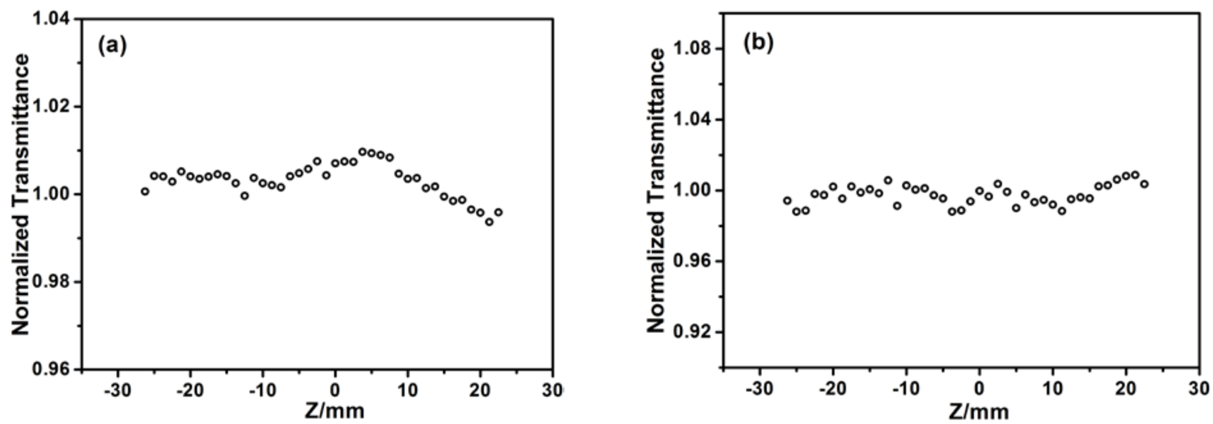

Figure S4. Open aperture curve (a) and closed aperture curve (b) for P_5W_{30} aqueous solution (1×10^{-3} mol·L^{-1}).

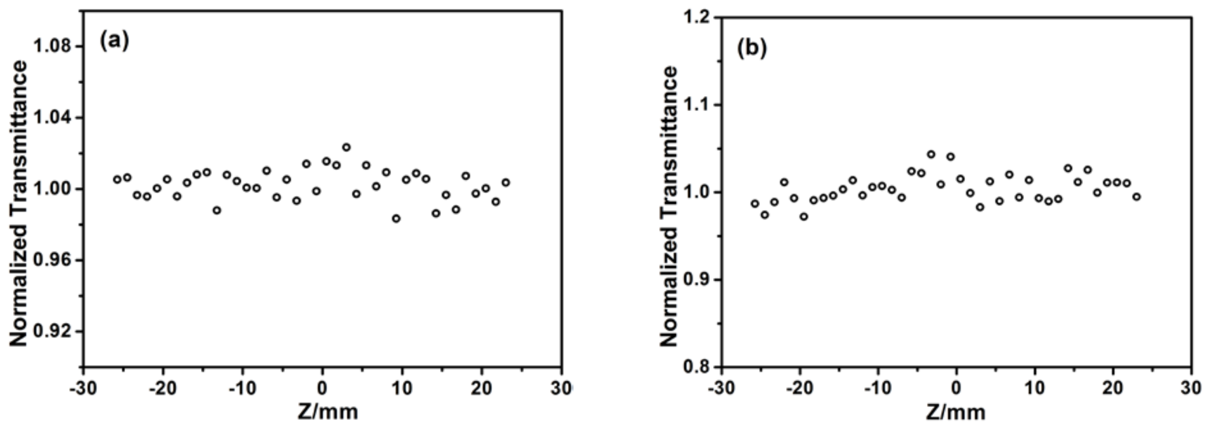

Figure S5. Open aperture curve (a) and closed aperture curve (b) for $(LDH/P_5W_{30})_{25}/LDH$ film.

REFERENCES

（1）Jiang, M.; Wang, E.; Xu, L.; Kang, Z.; Lian, S. The First Example of Multilayer Films with Thermochromicproperties. *J. Solid State Chem.* **2004,** *177,* 1776-1779.

（2）Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. Sensitive Measurement of Optical Nonlinearities Using a Single Beam. *IEEE J. Quantum. Elect.* **1990,** *26*, 760-769.