Supporting Information

Incorporation of Keplerate type Mo-O based macroanions into layered double hydrotalcite resulting in formation of all-inorganic composite films with remarkable third-order optical nonlinearities

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Preparation of (NH₄)₄₂[(Mo⁶⁺Mo₅⁵⁺O₂₁(H₂O)₆]₁₂{Mo₂⁺O₄(CH₃COO)}₃₀ ≈300H₂O·10CH₃COONH₄

The compound was prepared according to the literature method (Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Peters, F., Organizational Forms of Matter: An Inorganic Super Fullerene and Keplerate Based on Molybdenum Oxide. Angewandte Chemie International Edition 1998, 37, 3359-3363.). In a typical preparation, 5.6 g (NH₄)₆[Mo₇O₂₄]·4H₂O and 12.5 g CH₃COONH₄ was dissolved in 250 mL of water. The solution of 0.8 g N₂H₄·H₂SO₄ in water was added to the above solution, stirred for ten minutes and the colour of the solution changed to blue-green, followed by addition of 83 mL 50% (V/V) glacial acetic acid. After the reaction, the mixture was placed in an open conical flask at room temperature in a fume hood (the colour slowly turns to brown). Red-brown crystals were filtered off and the precipitate was washed with ethanol, finally dried and kept at room temperature for 4 days. Yield: 52% (based on ammonium molybdate).
Fig. S1 UV-vis spectrum of the aqueous solution of 
$(\text{NH}_4)_{42}[(\text{Mo}^{\text{VI}})\text{Mo}_{5}^{\text{VI}}\text{O}_{21}(\text{H}_2\text{O})_6]_{12}\{\text{Mo}_2\text{V}^{\text{O}}_4(\text{CH}_3\text{COO})_3\}_{30}] \approx 300\text{H}_2\text{O}-10\text{CH}_3\text{COONH}_4$

Zn$_2$Al-LDH preparation

The ZnAl-CO$_3$ and ZnAl-NO$_3$ LDH compounds were prepared according to the literature method (Zhao, J.; Kong, X.; Shi, W.; Shao, M.; Han, J.; Wei, M.; Evans, D. G.; Duan, X., Self-Assembly of Layered Double Hydroxide Nanosheets/Au Nanoparticles Ultrathin Films for Enzyme-Free Electrocatalysis of Glucose. *Journal of Materials Chemistry* **2011**, *21*, 13926-13933.). In a typical preparation, Zn(NO$_3$)$_2$·6H$_2$O (2 mmol), Al(NO$_3$)$_3$·9H$_2$O (1 mmol) and urea (12 mmol) were dissolved in 200 mL of water. The solution was heated and stirring for 24 hours at 100 °C. The obtained carbonate type LDH (Zn$_2$Al-CO$_3$) was washed with water and dried at 60 °C. The 0.1 g obtained Zn$_2$Al-CO$_3$ containing 0.15 mmol NaNO$_3$ is dispersed in 100 mL of aqueous solution containing 0.15 mmol NaNO$_3$ and CO$_2$ is removed, 31 uL concentrated HNO$_3$ was added and stirred under N$_2$ atmosphere for 24h, the ion exchange transformed to NO$_3^-$ form. The precipitated (Zn$_2$Al-NO$_3$) was isolated by centrifugation, washed with deionized water and dried at room temperature. The XRD patterns and SEM images of the resulting Zn$_2$Al-LDH were shown in Figs. S2 and S3, respectively, which are matching with the reported ones.
**Fig. S2** XRD patterns of Zn$_2$Al-CO$_3$ (red line) and ZnAl-NO$_3$ LDH (black line).

**Fig. S3** SEM images of Zn$_2$Al-LDH with different magnifications. Both the ZnAl-CO$_3$ LDH and ZnAl-NO$_3$ LDH show the same morphology.

**Zn$_2$Al-LDH exfoliation**

The exfoliation of ZnAl-NO$_3$ LDH was carried out according to the literature method (Li, L.; Ma, R.; Ebina, Y.; Iyi, N.; Sasaki, T., Positively Charged Nanosheets Derived Via Total Delamination of Layered Double Hydroxides. *Chemistry of materials* 2005, 17, 4386-4391.). In detail, the Zn$_2$Al-NO$_3$ (0.1 g) and 100 mL of formamide was added to the Erlenmeyer flask, stirred with a mechanical stirrer at 160 rpm under N$_2$ for two days. The resulting mixture was centrifuged at 3000 rpm for further 10 minutes to obtain a transparent and stable well-dispersed colloidal suspension.

The following formulas are used to calculate the third order nonlinear refractive index $n_2$ (esu), the nonlinear absorption coefficient $\beta$ (esu) and the third-order optical nonlinear

\[ \Delta T_{p-v} = 0.406(1 - S)^{0.25}\left| \Delta \phi_0 \right| \]  
\[ \Delta \phi_0 = k L_{\text{eff}} \gamma I_0 \]  
\[ L_{\text{eff}} = \left( 1 - e^{-\alpha_0 L} \right) / \alpha_0 \]  
\[ n_2 \text{(esu)} = \frac{cn_0}{40\pi} \gamma \text{(m}^2/\text{W}) \]  

where, $\Delta T_{p-v}$ is the normalized peak-valley difference, $\Delta \phi_0$ is the phase shift of the beam at the focus, $K = 2\pi/\lambda$ is the wave vector, $I_0$ (unit: W/m²) is the intensity of the light at focus, $L_{\text{eff}}$ is the effective length of the sample defined in terms of the linear-absorption coefficient $\alpha_0$ and the true optical path length through the sample, $n_0$ is the linear refractive index, and $\gamma$ is optical Kerr constant. The conversion can be realized between $n_2$ (esu) and $\gamma$ (m²/W) by equations (4).

When the sample is measured under open aperture, the normalized transmittance $T(z, s = 1)$ can be expressed as

\[ T(z, s = 1) = \sum_{m=0}^{\infty} \left[ -q_0(z) \right]^m \frac{1}{(m + 1)^{3/2}} \]  

where $q_0(z) = \beta I_0 L_{\text{eff}} / \left( 1 + z^2 / z_0^2 \right)$, $\beta$ is nonlinear absorption coefficient. From equation (5) we can get $\beta$. From equation (6), we can get the third-order optical nonlinear susceptibility $\chi^{(3)}$.

\[ \chi^{(3)} = \frac{cn_0^2 \gamma^2 + (c^2 \beta n_0^2 \lambda^2 / 64\pi^3)^2}{160\pi^2} \]  

\[ S4 \]
**Fig. S4** Z-scan curves of the Zn$_2$Al-NO$_3$ LDH suspension under open-aperture (a) and closed-aperture (b).

**Fig. S5** The XRD patterns of the composite films \((\text{Zn}_2\text{Al-LDH/\{Mo}_{132}\text{-Ac}\}}_n\) with number of layers; \(n = 12\) (red line) and \(n = 24\) (blue line), showing only wide peaks because of the fact that the materials deposited on the films are not thick enough.