1. Synthesis of Compounds 1, 3, 4

The compounds 1, 3 and 4 were synthesized and characterized exactly according to the literature \(^{[1-3]}\). Details are as follows

**Compound 1:** 0.8 g \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4 \) (6.1 mmol) was added to a solution of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\) (5.6 g, 4.5 mmol) and \(\text{CH}_3\text{COONH}_4\) (12.5 g, 162.2 mmol) in \(\text{H}_2\text{O}\) (250 mL). The solution was then stirred for 10 min (color changed to blue-green) and 50% \(\text{CH}_3\text{COOH}\) (83 mL) was added subsequently. The reaction solution, now green, was stored in an open 500-mL Erlenmeyer flask at 20°C without further stirring in a fume hood; slow color change to dark brown). After 4 d, the precipitate red-brown crystals of compound 1 were filtered off, washed with 90% ethanol, ethanol, and diethyl ether, and finally dried in air. Yield: 3.3 g (52% based on molybdate). IR data \(\nu/\text{cm}^{-1}\) (KBr): 1622 [m, \(\delta(\text{H}_2\text{O})\)], 1546 [m, \(\nu(\text{COO})\), \(\delta(\text{NH}_4^+)\)], 969 (m), 937 (w-m) [\(\nu(\text{Mo}=\text{O})\)], 855(m), 792(s), 628(w), 586 (s) and 463 (w). UV-Vis data: 453.5 nm in \(\text{H}_2\text{O}\), 461 nm in DMF/\(\text{H}_2\text{O}\) (4/1, volume ratio).

**Compound 3:** 0.25 g of compound 1 and 0.118 g of tetrabutylammonium bromide (corresponding to the mole ratio of 1:42) were dissolved in 15 ml of distilled water, respectively, and the pH values of both solutions were then adjusted to 4.2 by diluted acetic acid. The two solutions were then mixed under vigorous stirring. After 20 min of stirring, the resulting brown precipitate was isolated by filtration, washed with distilled water until the test of Br⁻ ions was negative. The product was dried in air. IR data \(\nu/\text{cm}^{-1}\) (KBr): 3439 [s, \(\delta(-\text{OH})\)], 2967 [s, \(\nu(\text{C}-\text{H}_3)\)], 1632 [m, \(\delta(\text{H}_2\text{O})\)], 1550 [m, \(\nu(\text{COO})\)], 1484 [m, \(\delta(\text{CH}_3)\)], and 1406 \(\delta(\text{CH}_3)\), \(\nu(\text{COO})\), \(\delta(\text{NH}_4^+)\)], 982 (s), 953 (w), 859 (w-m) [\(\nu(\text{Mo}=\text{O})\)], 804 (s), 731 (s), 635 (w), 577 (s). UV-Vis data: 462.5 nm in DMF/\(\text{H}_2\text{O}\) (4/1, volume ratio).

**Compound 4:** a freshly prepared aqueous solution of compound 1 was treated with a trichloromethane solution of the surfactant dimethyldioctadecylammonium bromide (DODA·Br). The initial ratio of DODA to compound 1 was 38:1, and the amount of surfactant was gradually increased until the aqueous phase became almost colorless. From the organic phase, a brownish material was isolated, which corresponds to the formula for compound 4: \((\text{DODA})_{40}\text{(NH}_4^+)_{2}[(\text{H}_2\text{O})_{3}\text{Mo}_{132}\text{O}_{372}\text{(CH}_3\text{COO})_{30}\text{(H}_2\text{O})_{72}]\). IR data \(\nu/\text{cm}^{-1}\) (KBr): 2922 [s, \(\nu(\text{C}-\text{H}_3)\)], 2852 [s, \(\nu(\text{C}-\text{H}_3)\)], 1557 [m, \(\nu(\text{COO})\)], 1466 [m, \(\delta(\text{CH}_3)\)], 1401\(\nu(\text{CH}_3)\), \(\nu(\text{COO})\), \(\delta(\text{NH}_4^+)\)], 1024, 981 (s), 956 (w), 859 (w-m) [\(\nu(\text{Mo}=\text{O})\)], 804 (s), 735 (s), 630 (w), 574 (s). UV-Vis data: 463.5 nm in \(\text{CHCl}_3\).
Fig.S1 FTIR spectra of the compounds 1 (a) and 2 (b)

Fig.S1 shows the comparative IR spectra of compounds 1 and 2. The weak band at 2946 and 1484 cm$^{-1}$ in compound 2 are assigned to the stretching and bent vibration of –C–H of –CH$_3$ moiety that corresponds to the tetramethylammonium (TMA) cations respectively. All other characteristic bands for the spherical structures match well with those of compound 1. Compound 2 shows bands at 1625 [m, $\delta$(H$_2$O)], 1545 [m, $\nu$ (COO)], 1484 (m) [$\delta$(CH$_3$)], and 1407 [(m) (COO), ($\delta_{as}$(NH$_4^+$)]), 970 (s), 852 (w-m)(Mo=O), 796 (s), 724 (s), 631 (w), 568(s) and 462 (w) which are almost similar to those of compound 1, i.e., at 1622[m,$\delta$(H$_2$O)], 1546 [m, $\nu$(COO)], 1403 [(m) (COO), ($\delta_{as}$(NH$_4^+$)], 969(m), 937 (w-m)(Mo=O), 855(m), 792(s), 723(s), 628(w), 568(s) and 463 (w). These are the characteristic bands for the Keplerate type molybdenum-oxide based polyoxometalates. Therefore we confirm from the spectra that compound 2 has the same [Mo$_{132}$O$_{372}$(CH$_3$COO)$_{30}$(H$_2$O)$_{72}$]$^{42-}$ anions\cite{1}.

Fig.S2 TG (a)/DTA (b) curves of compound 2

As shown in Fig.S2, compound 2 loses its mass via three steps. The first mass loss of 12.5% (calcld. 12.5%) in the temperature range of 25 - 150 °C with a corresponding exothermal peak at 62.4°C in DTA curve is assigned to the loss of 189 water molecules; the second mass loss of 4.7% (calcld. 4.7%) in the temperature range of 150 - 290 °C with a strong corresponding endothermal peak at 258.3 °C in DTA curve, is assigned to the loss of 72 water ligands. The third mass loss of 14.4% (calcld. 16.0%) in the temperature range of 290 - 600°C with a corresponding exothermal peak at 387.2 °C in DTA curve is assigned to the thermal decomposition of the rest organic moieties and the polyoxometalate components, leading to the formation of the corresponding MoO$_3$. Above 600 °C, the Mo-O frame decomposes. We can see from the above contents that the molecule formula matches well with the TG analysis.
3. UV-vis spectra of compounds 1-4

![UV-vis spectra of compounds 1-4](image)

Fig. S3  UV-Vis. spectra of compound 1 in water (A), compound 1 - 3 in DMF/H₂O (4/1, volume ratio) [(B) - (D), and compound 4 in chloroform (E)]

The concentrations of all solutions were 5×10⁻⁶ mol/L.

4. Calculation Formulas of Third-order Nonlinear Optical Parameters

The nonlinear refractive index \(n_2\) (esu), nonlinear absorption coefficient \(\beta\) (esu) and the resulting third-order optical nonlinear (NLO) susceptibility \(\chi^{(3)}\) (esu) have been calculated according to following equations\[^{4,5}\].

\[
\Delta T_{p-V} = 0.406(1 - S)^{0.25}\left|\Delta \phi_0\right| 
\]  

\[
\Delta \phi_0 = kL_{\text{eff}}I_0 
\]
\[
L_{\text{eff}} = \left(1 - e^{-a_0 L}\right) / a_0
\]  
(3)

\[
n_2(\text{esu}) = \frac{cN_0 \gamma}{40\pi} \left(\text{m}^2 / \text{W}\right)
\]  
(4)

\[
\text{Re} \chi^{(3)} \left(\frac{m^2}{\nu^2}\right) = \frac{4\pi}{3\nu^2} \times 10^{-8} n_2(\text{esu})
\]  
(5)

\[
\text{Im} \chi^{(3)} \left(\frac{m^2}{\nu^2}\right) = \frac{4\pi}{3\nu^2} \times 10^{-8} \beta(\text{esu})
\]  
(6)

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/m\(^2\)) 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 \(a_0\) 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 \(n_2(\text{esu})\) and \(\gamma(\text{m}^2/\text{W})\) by Eq (4).

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

\[
T(z, s=1) = \sum_{m=0}^{\infty} \left[\frac{-q_0(z)}{m+1}\right]^{m/2}
\]  
(7)

where \(q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z^2 / z_0^2)\), \(\beta\) is nonlinear absorption coefficient.

From Eq (7), we can get \(\beta\). From Eq (8), we can get the third-order optical nonlinear susceptibility \(\chi^{(3)}\).

\[
\chi^{(3)} \left(\frac{m^2}{\nu^2}\right) = \sqrt{\left(\text{Re} \chi^{(3)} \left(\frac{m^2}{\nu^2}\right)\right)^2 + \left(\text{Im} \chi^{(3)} \left(\frac{m^2}{\nu^2}\right)\right)^2}
\]  
(8)

5. Z-Scan Curves of Solvents and Ammonium Salts Used;

Fig.S4  Z-Scan curves of ammonium bromide in DMF/H\(_2\)O (volume ratio 4/1, 1×10\(^{-5}\) mol/L)

(A) Open-aperture curve; (B) closed-aperture curve.
**Fig. S5**  Z-Scan curves of tetramethylammonium bromide in DMF/H$_2$O (volume ratio 4/1, 1×10$^{-5}$ mol/L)

(A) Open-aperture curve; (B) closed-aperture curve.

**Fig. S6**  Z-Scan curves of DODA bromide in chloroform (1×10$^{-5}$ mol/L)

(A) Open-aperture curve; (B) closed-aperture curve.

**Fig. S7**  Z-Scan curves of the DMF/H$_2$O (volume ratio 4/1) mixed solvent

(A) Open-aperture curve; (B) closed-aperture curve.
Fig. S8  Z-Scan curves of chloroform

(A) Open-aperture curve; (B) closed-aperture curve.

Reference