Supporting Information

Two New Isolated Zn-*ε*-Keggin Clusters Modified by Conjugated Organic Ligands with Decent Electrocatalytic and Third-Order NLO Properties

Xiao-Mei Liu, Fan-Qiong Meng, Wei-Wei Cheng, Jia-Peng Cao, Ji-Lei Wang, Ting-Ting Zang, Qing-Dong Ping, Hui Xie and Yan Xu*[a]

[a] College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, P.R. China.

Details of third-order NLO properties for two compounds

The sample of compounds **1**-**2** were dissolved in DMSO solution with the concentration of 1.0× 10^{-4} mol L^{-1} and determined under a laser wavelength of 760 nm. The filled squares represent the experimental data, and the solid lines are the theoretical simulated curve based on the following equations:

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

$$q_0(z) = \frac{\beta I_0 L_{eff}}{1 + x^2} \quad (2)$$

I_0 is the input intensity at the focus z = 0 and equals the input energy divided by $\pi\omega_0^2$, and L_{eff} is the effective length, in which L is the sample length and α is the linear absorption coefficient. Where $x = z/z_0$, $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam, where z is the sample position, ω_0 is the spot size at the focus, and λ is the wavelength of the beam. By using the above equations, we obtain the nonlinear absorption coefficient β. Furthermore, the molecular TPA cross section σ can be determined by the following relationship:

$$\sigma = h\nu\beta / N_A d \times 10^{-3} \quad (3)$$

Here, h is the Planck's constant, v is the frequency of input intensity, N_A is the Avogadro's constant, and d is the concentration of the complex.

Structure

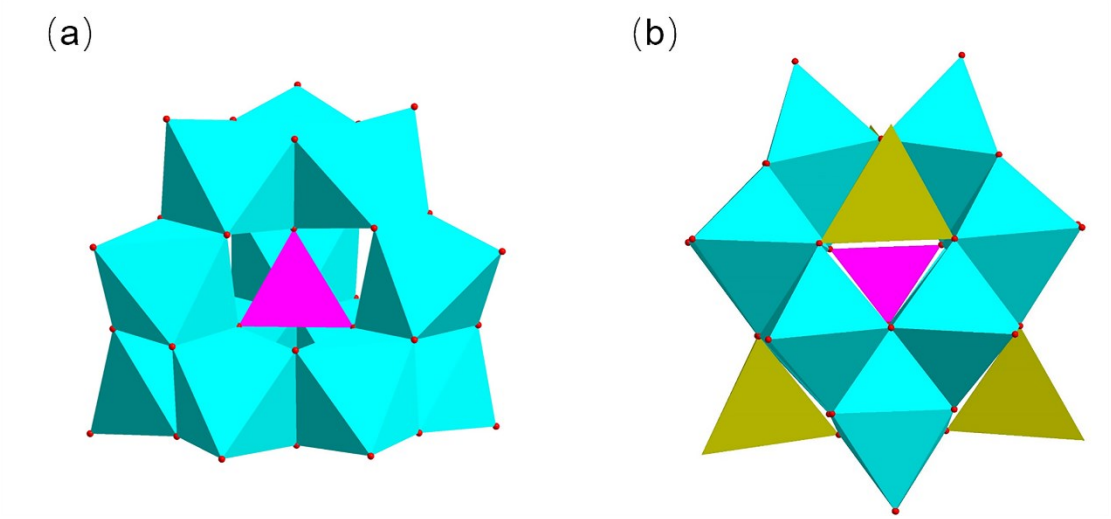


Fig. S1 Polyhedral representation of ε-Keggin-type polyoxometalate (a) and Zn_4-ε-Keggin unit (b). Color codes: P, purple; Mo, blue; Zn, yellow; O, red.

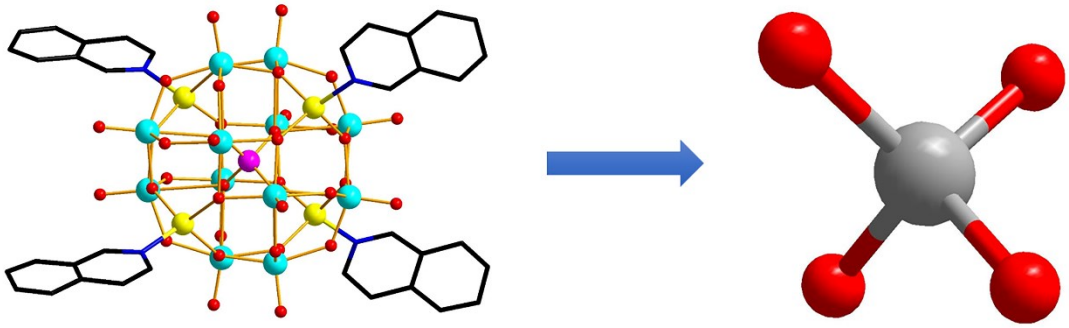


Fig. S2 Ball-and-stick representation of compound **1** and SiO_4. Color codes: P, purple; Mo, blue; Zn, yellow; O, red; Si, grey.

PXRD patterns

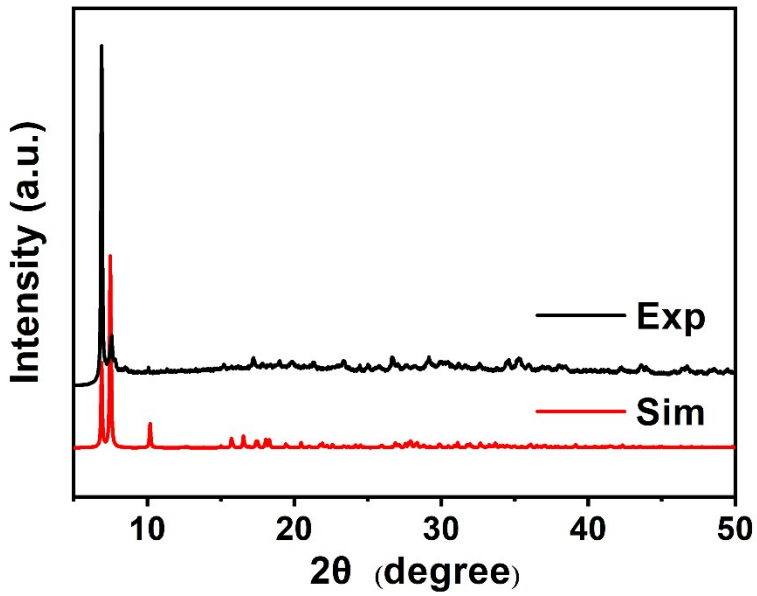


Fig. S3 Experimental and simulated PXRD patterns of compound **1**.

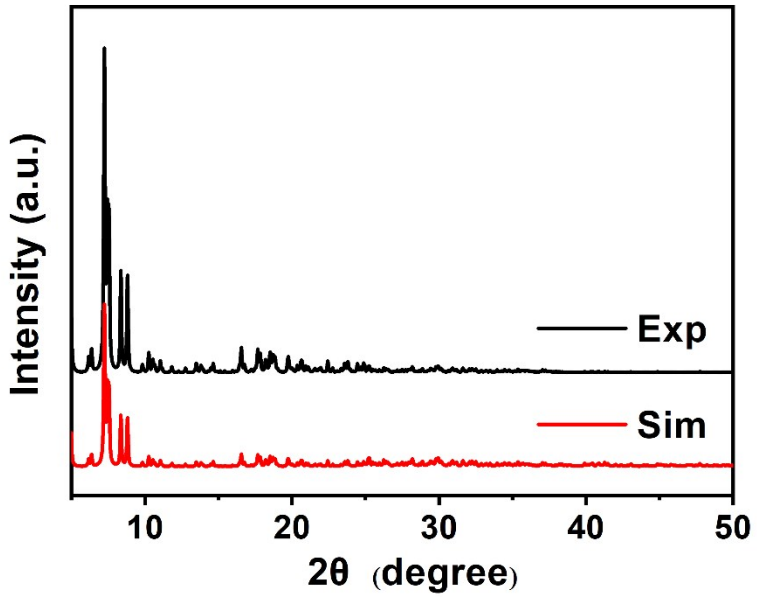


Fig. S4 Experimental and simulated patterns of compound **2**.

IR spectra

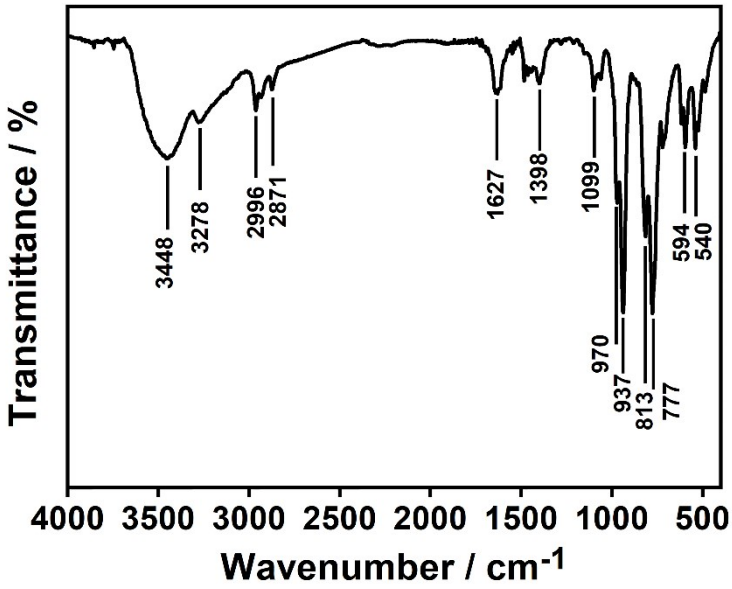


Fig. S5 The IR spectra of compound **1**.

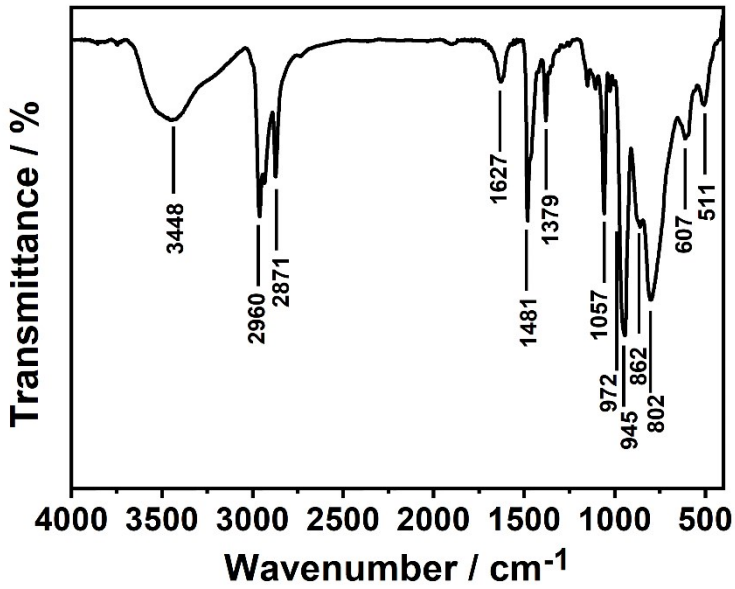


Fig. S6 The IR spectra of compound **2**.

TG

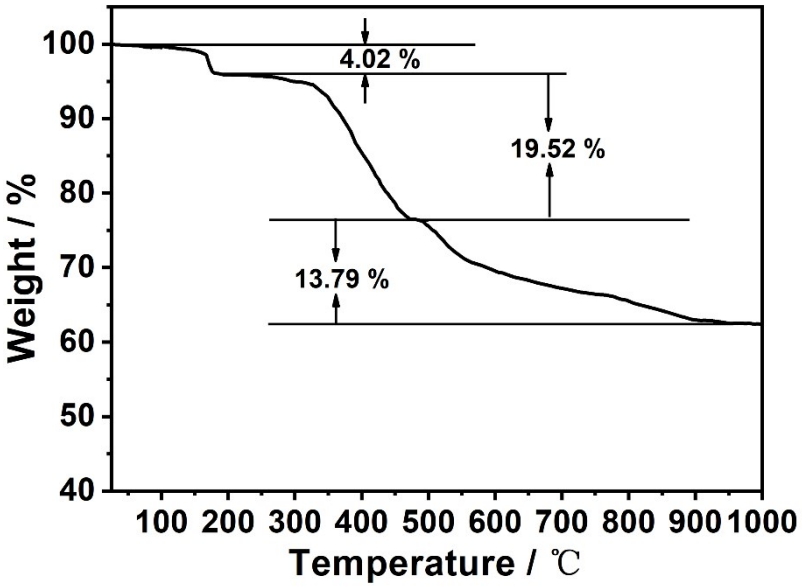


Fig. S7 The TG curve of compound **1**.

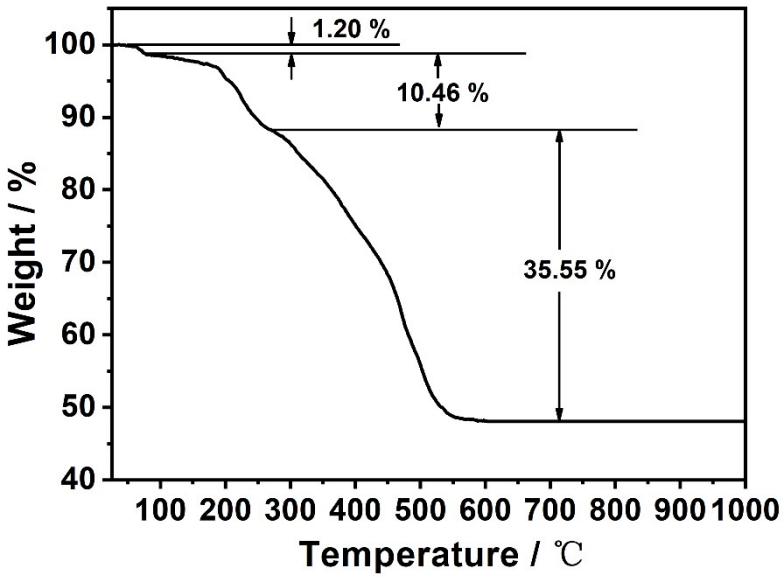


Fig. S8 The TG curve of compound **2**.

UV-Vis

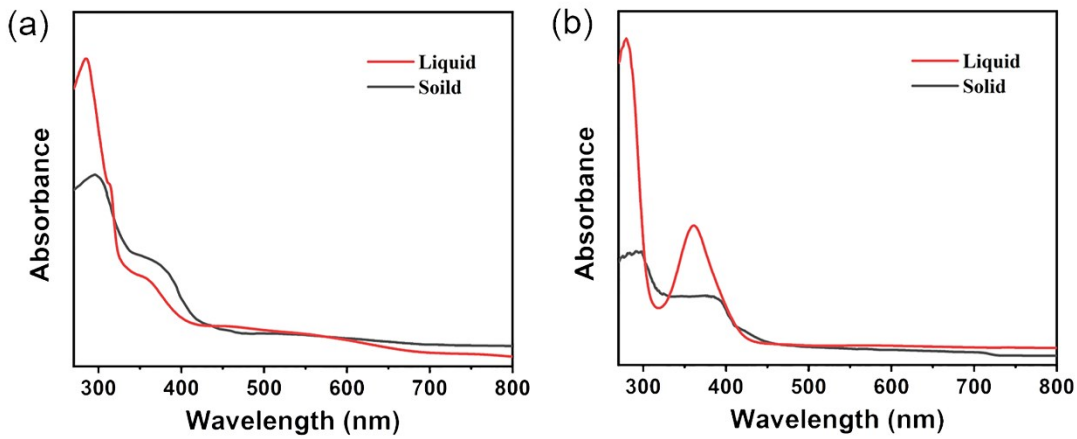


Fig. S9 The UV-Vis spectra in 270-800 nm range of solid and solution (in DMSO) for compound **1 (a)** and compound **2 (b).**

For compound **1** (Fig. S9a), the UV-Vis spectra of solid and solution (in DMSO) display two absorption peaks with a range of 270−320 and 350−450 nm, respectively. Perfect overlapping between liquid UV and solid UV shows that compound **1** is stable in solution phase. Similarly, compound **2** is also stable in DMSO as shown in Fig. S9b.

^{31}P NMR

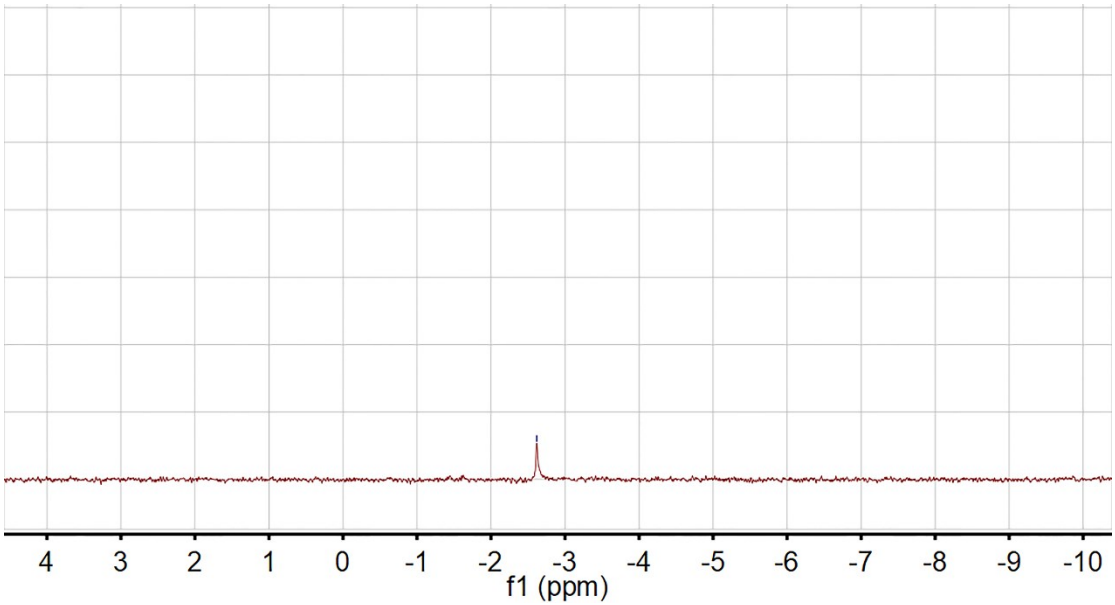


Fig. S10 ^{31}P NMR spectra of compound **1** dissolved in DMSO-D6 at room temperature.

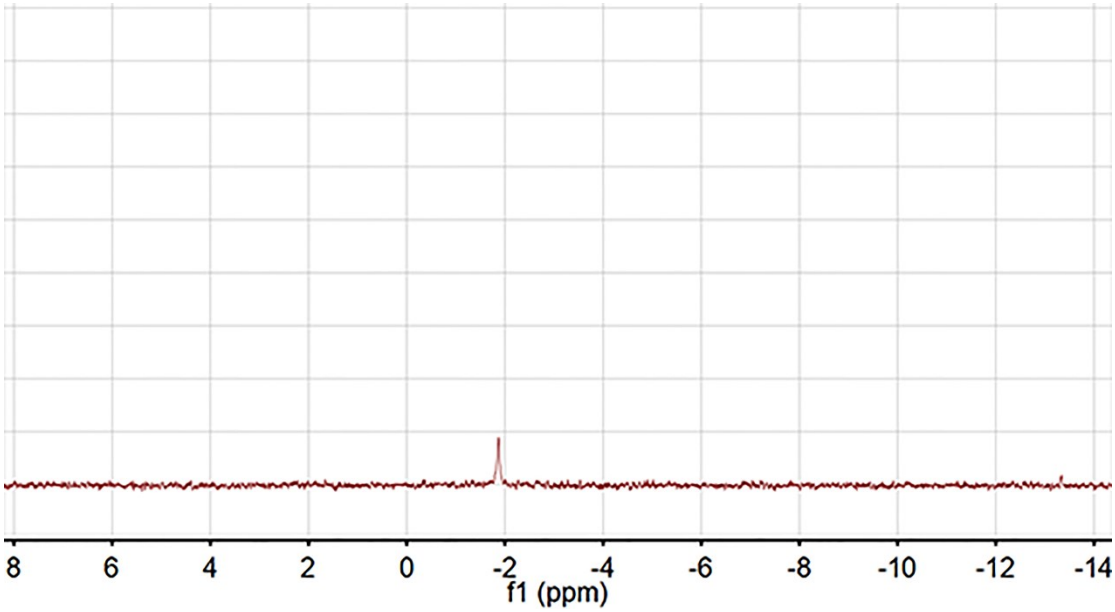


Fig. S11 ^{31}P NMR spectra of compound **2** dissolved in DMSO-D6 at room temperature.

The ^{31}P NMR spectra of compounds **1** and **2** dissolved in DMSO both reveal only one resonance at around δ = 2 ppm (Fig. S10 and S11), which indicates only one type of P in the both compounds, and further demonstrates that the two compounds are stable in DMSO solution.

Table S1. Selected bond lengths (Å) for compound **1**.

Mo(1)-O(20)	1.653(13)	Mo(4)-O(13)	2.051(12)
Mo(1)-O(8)	1.827(12)	Mo(5)-O(19)	1.682(13)
Mo(1)-O(7)	1.829(12)	Mo(5)-O(14)	1.962(12)
Mo(1)-O(10)	1.995(11)	Mo(5)-O(4)	1.968(13)
Mo(1)-O(10)#1	2.000(11)	Mo(5)-O(3)	1.977(11)
Mo(2)-O(15)	1.645(12)	Mo(5)-O(9)#1	1.999(12)
Mo(2)-O(2)	1.965(13)	Mo(5)-O(5)	2.504(10)
Mo(2)-O(14)#1	1.972(12)	Mo(6)-O(18)	1.684(13)
Mo(2)-O(1)	1.974(11)	Mo(6)-O(12)	1.825(12)
Mo(2)-O(12)	2.019(12)	Mo(6)-O(9)	1.850(12)
Mo(3)-O(17)	1.677(14)	Mo(6)-O(11)	2.003(12)
Mo(3)-O(4)	1.944(12)	Mo(6)-O(11)#1	2.013(11)
Mo(3)-O(3)	1.961(13)	Zn(7)-O(2)#1	1.948(13)
Mo(3)-O(8)	1.990(13)	Zn(7)-O(4)	1.952(13)
Mo(3)-O(13)	2.045(12)	Zn(7)-O(10)	1.970(12)
Mo(3)-O(6)	2.503(11)	Zn(7)-N(2)	2.029(15)
Mo(4)-O(16)	1.657(13)	Zn(8)-O(11)	1.946(13)
Mo(4)-O(1)	1.927(13)	Zn(8)-O(3)	1.975(12)
Mo(4)-O(2)	1.955(11)	Zn(8)-N(1)	1.986(16)
Mo(4)-O(7)	2.019(13)	Zn(8)-O(1)	1.986(12)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, z.

Table S2. Selected bond lengths (Å) for compound **2**.

Mo(1)-O(36)	1.687(4)	Mo(9)-O(27)	1.828(4)
Mo(1)-O(23)	1.945(4)	Mo(9)-O(16)	1.846(4)
Mo(1)-O(13)	1.973(4)	Mo(9)-O(17)	1.993(4)
Mo(1)-O(4)	1.975(4)	Mo(9)-O(8)	2.015(4)
Mo(1)-O(33)	2.042(4)	Mo(10)-O(21)	1.699(4)
Mo(1)-O(34)	2.494(4)	Mo(10)-O(29)	1.811(4)
Mo(2)-O(37)	1.679(4)	Mo(10)-O(41)	1.820(4)
Mo(2)-O(6)	1.964(4)	Mo(10)-O(3)	2.000(4)
Mo(2)-O(5)	1.965(4)	Mo(10)-O(1)	2.005(4)
Mo(2)-O(14)	2.007(4)	Mo(11)-O(39)	1.668(4)
Mo(2)-O(9)	2.075(4)	Mo(11)-O(2)	1.957(4)
Mo(3)-O(20)	1.702(4)	Mo(11)-O(10)	1.971(4)
Mo(3)-O(25)	1.825(4)	Mo(11)-O(27)	1.998(4)
Mo(3)-O(14)	1.827(4)	Mo(11)-O(30)	2.100(4)
Mo(3)-O(17)	1.969(4)	Mo(12)-O(35)	1.672(4)
Mo(3)-O(8)	2.027(4)	Mo(12)-O(32)	1.955(4)
Mo(4)-O(28)	1.678(4)	Mo(12)-O(15)	1.976(4)
Mo(4)-O(32)	1.933(4)	Mo(12)-O(12)	1.983(4)
Mo(4)-O(10)	1.986(4)	Mo(12)-O(41)	2.029(4)
Mo(4)-O(2)	1.987(4)	Zn(1)-O(5)	2.020(4)
Mo(4)-O(29)	2.048(4)	Zn(1)-O(8)	2.037(4)
Mo(4)-O(26)	2.510(4)	Zn(1)-O(4)	2.114(4)
Mo(5)-O(18)	1.675(4)	Zn(1)-N(2)	2.131(5)
Mo(5)-O(13)	1.948(4)	Zn(1)-N(1)	2.256(5)
Mo(5)-O(4)	1.960(4)	Zn(2)-O(1)	1.934(4)
Mo(5)-O(16)	2.034(4)	Zn(2)-O(13)	1.952(4)
Mo(5)-O(30)	2.108(4)	Zn(2)-O(19)	1.953(4)
Mo(5)-O(11)	2.452(4)	Zn(2)-O(2)	1.963(4)
Mo(6)-O(40)	1.676(4)	Zn(3)-O(12)	2.029(4)
Mo(6)-O(12)	1.952(4)	Zn(3)-O(10)	2.035(4)
Mo(6)-O(15)	1.967(4)	Zn(3)-O(17)	2.100(4)
Mo(6)-O(25)	2.022(4)	Zn(3)-N(8)	2.170(5)
Mo(6)-O(9)	2.080(4)	Zn(3)-N(7)	2.177(5)
Mo(7)-O(31)	1.685(4)	Zn(4)-O(15)	2.039(4)
Mo(7)-O(23)	1.946(4)	Zn(4)-O(6)	2.056(4)
Mo(7)-O(5)	1.970(4)	Zn(4)-O(3)	2.069(4)
Mo(7)-O(6)	1.986(4)	Zn(4)-N(9)	2.188(5)

Mo(7)-O(22)	2.042(4)	Zn(4)-N(10)	2.202(5)
Mo(8)-O(38)	1.694(4)	Zn(5)-N(4)	2.073(5)
Mo(8)-O(33)	1.820(4)	Zn(5)-N(5)	2.083(6)
Mo(8)-O(22)	1.821(4)	Zn(5)-N(3)	2.089(6)
Mo(8)-O(3)	1.997(4)	Zn(5)-O(42)	2.126(5)
Mo(8)-O(1)	2.031(4)	Zn(5)-N(6)	2.129(6)
Mo(9)-O(24)	1.689(4)	Zn(5)-O(19)	2.450(4)

Table S3. Selected bond angles (°) for compound **1**.

O(20)-Mo(1)-O(8)	103.6(6)	O(16)-Mo(4)-O(13)	99.8(6)
O(20)-Mo(1)-O(7)	103.9(6)	O(1)-Mo(4)-O(13)	85.4(5)
O(8)-Mo(1)-O(7)	98.1(6)	O(2)-Mo(4)-O(13)	153.6(5)
O(20)-Mo(1)-O(10)	102.2(6)	O(7)-Mo(4)-O(13)	85.4(5)
O(8)-Mo(1)-O(10)	88.6(5)	O(19)-Mo(5)-O(14)	100.3(6)
O(7)-Mo(1)-O(10)	150.6(5)	O(19)-Mo(5)-O(4)	107.0(6)
O(20)-Mo(1)-O(10)#1	103.0(6)	O(14)-Mo(5)-O(4)	87.8(5)
O(8)-Mo(1)-O(10)#1	150.7(5)	O(19)-Mo(5)-O(3)	103.5(6)
O(7)-Mo(1)-O(10)#1	87.3(5)	O(14)-Mo(5)-O(3)	154.9(5)
O(10)-Mo(1)-O(10)#1	73.8(5)	O(4)-Mo(5)-O(3)	92.7(5)
O(15)-Mo(2)-O(2)	105.4(6)	O(19)-Mo(5)-O(9)#1	98.0(6)
O(15)-Mo(2)-O(14)#1	100.2(6)	O(14)-Mo(5)-O(9)#1	85.5(5)
O(2)-Mo(2)-O(14)#1	87.4(5)	O(4)-Mo(5)-O(9)#1	154.9(5)
O(15)-Mo(2)-O(1)	105.8(6)	O(3)-Mo(5)-O(9)#1	83.4(5)
O(2)-Mo(2)-O(1)	91.6(5)	O(19)-Mo(5)-O(5)	171.1(5)
O(14)#1-Mo(2)-O(1)	153.3(5)	O(14)-Mo(5)-O(5)	74.9(4)
O(15)-Mo(2)-O(12)	101.3(6)	O(4)-Mo(5)-O(5)	80.5(4)
O(2)-Mo(2)-O(12)	153.1(5)	O(3)-Mo(5)-O(5)	80.4(4)
O(14)#1-Mo(2)-O(12)	85.2(5)	O(9)#1-Mo(5)-O(5)	74.3(4)
O(1)-Mo(2)-O(12)	83.7(5)	O(18)-Mo(6)-O(12)	102.4(6)
O(17)-Mo(3)-O(4)	106.7(6)	O(18)-Mo(6)-O(9)	105.0(6)
O(17)-Mo(3)-O(3)	103.4(6)	O(12)-Mo(6)-O(9)	97.9(5)
O(4)-Mo(3)-O(3)	94.0(5)	O(18)-Mo(6)-O(11)	101.3(6)
O(17)-Mo(3)-O(8)	101.6(6)	O(12)-Mo(6)-O(11)	88.9(5)
O(4)-Mo(3)-O(8)	84.4(5)	O(9)-Mo(6)-O(11)	150.7(5)
O(3)-Mo(3)-O(8)	154.3(5)	O(18)-Mo(6)-O(11)#1	103.3(6)
O(17)-Mo(3)-O(13)	97.3(6)	O(12)-Mo(6)-O(11)#1	151.5(5)
O(4)-Mo(3)-O(13)	155.3(5)	O(9)-Mo(6)-O(11)#1	87.2(5)
O(3)-Mo(3)-O(13)	85.9(5)	O(11)-Mo(6)-O(11)#1	74.2(5)
O(8)-Mo(3)-O(13)	85.2(5)	O(2)#1-Zn(7)-O(4)	100.1(5)
O(17)-Mo(3)-O(6)	170.0(6)	O(2)#1-Zn(7)-O(10)	112.4(5)
O(4)-Mo(3)-O(6)	81.7(4)	O(4)-Zn(7)-O(10)	112.5(5)
O(3)-Mo(3)-O(6)	81.0(4)	O(2)#1-Zn(7)-N(2)	114.0(6)
O(8)-Mo(3)-O(6)	73.4(4)	O(4)-Zn(7)-N(2)	114.1(6)
O(13)-Mo(3)-O(6)	73.9(4)	O(10)-Zn(7)-N(2)	104.1(6)
O(16)-Mo(4)-O(1)	107.1(6)	O(11)-Zn(8)-O(3)	112.0(5)
O(16)-Mo(4)-O(2)	105.7(6)	O(11)-Zn(8)-N(1)	102.1(6)

O(1)-Mo(4)-O(2)	93.3(5)	O(3)-Zn(8)-N(1)	117.0(6)
O(16)-Mo(4)-O(7)	99.8(6)	O(11)-Zn(8)-O(1)	114.3(5)
O(1)-Mo(4)-O(7)	152.7(5)	O(3)-Zn(8)-O(1)	101.5(5)
O(2)-Mo(4)-O(7)	83.7(5)	N(1)-Zn(8)-O(1)	110.4(6)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, z.

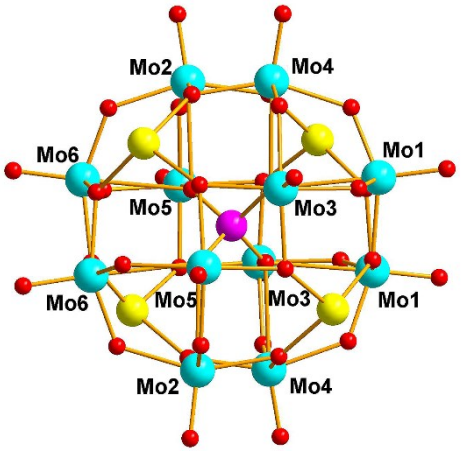
Table S4. Selected bond angles (°) for compound **2**.

O(36)-Mo(1)-O(23)	100.96(18)	O(22)-Mo(8)-O(1)	153.12(16)
O(36)-Mo(1)-O(13)	104.25(18)	O(3)-Mo(8)-O(1)	73.81(15)
O(23)-Mo(1)-O(13)	153.11(15)	O(24)-Mo(9)-O(27)	103.29(18)
O(36)-Mo(1)-O(4)	107.18(18)	O(24)-Mo(9)-O(16)	104.61(18)
O(23)-Mo(1)-O(4)	88.51(15)	O(27)-Mo(9)-O(16)	97.99(17)
O(13)-Mo(1)-O(4)	92.86(15)	O(24)-Mo(9)-O(17)	101.87(18)
O(36)-Mo(1)-O(33)	99.64(18)	O(27)-Mo(9)-O(17)	86.74(15)
O(23)-Mo(1)-O(33)	84.89(16)	O(16)-Mo(9)-O(17)	151.17(15)
O(13)-Mo(1)-O(33)	81.83(15)	O(24)-Mo(9)-O(8)	101.65(18)
O(4)-Mo(1)-O(33)	153.14(15)	O(27)-Mo(9)-O(8)	151.81(15)
O(36)-Mo(1)-O(34)	172.64(16)	O(16)-Mo(9)-O(8)	88.20(16)
O(23)-Mo(1)-O(34)	75.52(14)	O(17)-Mo(9)-O(8)	75.41(15)
O(13)-Mo(1)-O(34)	78.35(14)	O(21)-Mo(10)-O(29)	105.62(18)
O(4)-Mo(1)-O(34)	79.38(13)	O(21)-Mo(10)-O(41)	102.75(18)
O(33)-Mo(1)-O(34)	73.76(13)	O(29)-Mo(10)-O(41)	98.50(17)
O(37)-Mo(2)-O(6)	105.45(18)	O(21)-Mo(10)-O(3)	102.05(18)
O(37)-Mo(2)-O(5)	103.78(18)	O(29)-Mo(10)-O(3)	149.72(15)
O(6)-Mo(2)-O(5)	95.47(15)	O(41)-Mo(10)-O(3)	87.03(16)
O(37)-Mo(2)-O(14)	101.49(17)	O(21)-Mo(10)-O(1)	101.13(17)
O(6)-Mo(2)-O(14)	152.04(15)	O(29)-Mo(10)-O(1)	88.43(16)
O(5)-Mo(2)-O(14)	85.16(15)	O(41)-Mo(10)-O(1)	152.26(16)
O(37)-Mo(2)-O(9)	97.91(18)	O(3)-Mo(10)-O(1)	74.29(15)
O(6)-Mo(2)-O(9)	87.14(15)	O(39)-Mo(11)-O(2)	104.54(18)
O(5)-Mo(2)-O(9)	156.56(15)	O(39)-Mo(11)-O(10)	104.96(19)
O(14)-Mo(2)-O(9)	81.87(15)	O(2)-Mo(11)-O(10)	95.59(15)
O(20)-Mo(3)-O(25)	103.67(18)	O(39)-Mo(11)-O(27)	101.18(18)
O(20)-Mo(3)-O(14)	105.03(18)	O(2)-Mo(11)-O(27)	153.43(15)
O(25)-Mo(3)-O(14)	97.58(17)	O(10)-Mo(11)-O(27)	83.99(15)
O(20)-Mo(3)-O(17)	103.18(17)	O(39)-Mo(11)-O(30)	97.48(18)
O(25)-Mo(3)-O(17)	87.91(16)	O(2)-Mo(11)-O(30)	83.29(15)
O(14)-Mo(3)-O(17)	149.02(16)	O(10)-Mo(11)-O(30)	157.03(15)
O(20)-Mo(3)-O(8)	100.08(17)	O(27)-Mo(11)-O(30)	86.94(15)
O(25)-Mo(3)-O(8)	153.66(16)	O(35)-Mo(12)-O(32)	101.66(18)
O(14)-Mo(3)-O(8)	87.01(16)	O(35)-Mo(12)-O(15)	105.12(19)
O(17)-Mo(3)-O(8)	75.64(15)	O(32)-Mo(12)-O(15)	151.81(15)
O(28)-Mo(4)-O(32)	101.80(18)	O(35)-Mo(12)-O(12)	105.16(18)
O(28)-Mo(4)-O(10)	103.81(18)	O(32)-Mo(12)-O(12)	87.29(15)

O(32)-Mo(4)-O(10)	88.58(15)	O(15)-Mo(12)-O(12)	94.04(15)
O(28)-Mo(4)-O(2)	104.26(18)	O(35)-Mo(12)-O(41)	99.76(18)
O(32)-Mo(4)-O(2)	152.30(15)	O(32)-Mo(12)-O(41)	84.54(15)
O(10)-Mo(4)-O(2)	94.17(15)	O(15)-Mo(12)-O(41)	82.43(15)
O(28)-Mo(4)-O(29)	100.64(17)	O(12)-Mo(12)-O(41)	154.87(15)
O(32)-Mo(4)-O(29)	84.32(15)	O(5)-Zn(1)-O(8)	104.61(15)
O(10)-Mo(4)-O(29)	155.46(15)	O(5)-Zn(1)-O(4)	88.30(15)
O(2)-Mo(4)-O(29)	81.82(15)	O(8)-Zn(1)-O(4)	96.39(15)
O(28)-Mo(4)-O(26)	173.22(16)	O(5)-Zn(1)-N(2)	132.77(17)
O(32)-Mo(4)-O(26)	74.11(14)	O(8)-Zn(1)-N(2)	122.62(17)
O(10)-Mo(4)-O(26)	81.68(14)	O(4)-Zn(1)-N(2)	86.75(16)
O(2)-Mo(4)-O(26)	79.02(14)	O(5)-Zn(1)-N(1)	95.37(16)
O(29)-Mo(4)-O(26)	73.78(13)	O(8)-Zn(1)-N(1)	103.19(16)
O(18)-Mo(5)-O(13)	104.83(18)	O(4)-Zn(1)-N(1)	158.43(16)
O(18)-Mo(5)-O(4)	105.79(18)	N(2)-Zn(1)-N(1)	75.15(17)
O(13)-Mo(5)-O(4)	94.08(15)	O(1)-Zn(2)-O(13)	110.69(16)
O(18)-Mo(5)-O(16)	98.03(17)	O(1)-Zn(2)-O(19)	113.21(17)
O(13)-Mo(5)-O(16)	156.10(15)	O(13)-Zn(2)-O(19)	106.96(17)
O(4)-Mo(5)-O(16)	86.26(15)	O(1)-Zn(2)-O(2)	111.86(16)
O(18)-Mo(5)-O(30)	97.29(18)	O(13)-Zn(2)-O(2)	103.57(16)
O(13)-Mo(5)-O(30)	84.44(15)	O(19)-Zn(2)-O(2)	110.01(17)
O(4)-Mo(5)-O(30)	156.42(15)	O(12)-Zn(3)-O(10)	93.61(15)
O(16)-Mo(5)-O(30)	85.83(15)	O(12)-Zn(3)-O(17)	99.24(15)
O(18)-Mo(5)-O(11)	170.24(17)	O(10)-Zn(3)-O(17)	98.15(15)
O(13)-Mo(5)-O(11)	80.06(14)	O(12)-Zn(3)-N(8)	89.66(17)
O(4)-Mo(5)-O(11)	82.00(14)	O(10)-Zn(3)-N(8)	99.32(17)
O(16)-Mo(5)-O(11)	76.32(13)	O(17)-Zn(3)-N(8)	159.82(16)
O(30)-Mo(5)-O(11)	74.55(13)	O(12)-Zn(3)-N(7)	132.12(18)
O(40)-Mo(6)-O(12)	105.87(19)	O(10)-Zn(3)-N(7)	133.04(17)
O(40)-Mo(6)-O(15)	104.79(18)	O(17)-Zn(3)-N(7)	85.92(17)
O(12)-Mo(6)-O(15)	95.31(15)	N(8)-Zn(3)-N(7)	74.78(18)
O(40)-Mo(6)-O(25)	101.68(17)	O(15)-Zn(4)-O(6)	93.33(15)
O(12)-Mo(6)-O(25)	83.26(15)	O(15)-Zn(4)-O(3)	99.09(15)
O(15)-Mo(6)-O(25)	152.82(15)	O(6)-Zn(4)-O(3)	99.17(14)
O(40)-Mo(6)-O(9)	96.95(19)	O(15)-Zn(4)-N(9)	95.37(17)
O(12)-Mo(6)-O(9)	155.71(15)	O(6)-Zn(4)-N(9)	95.37(17)
O(15)-Mo(6)-O(9)	86.65(15)	O(3)-Zn(4)-N(9)	158.79(16)
O(25)-Mo(6)-O(9)	84.09(14)	O(15)-Zn(4)-N(10)	133.36(16)

O(31)-Mo(7)-O(23)	100.55(18)	O(6)-Zn(4)-N(10)	132.33(16)
O(31)-Mo(7)-O(5)	104.81(18)	O(3)-Zn(4)-N(10)	84.40(16)
O(23)-Mo(7)-O(5)	86.94(15)	N(9)-Zn(4)-N(10)	74.39(18)
O(31)-Mo(7)-O(6)	104.22(18)	N(4)-Zn(5)-N(5)	115.1(2)
O(23)-Mo(7)-O(6)	153.86(15)	N(4)-Zn(5)-N(3)	79.3(2)
O(5)-Mo(7)-O(6)	94.62(15)	N(5)-Zn(5)-N(3)	107.1(3)
O(31)-Mo(7)-O(22)	99.01(17)	N(4)-Zn(5)-O(42)	148.9(2)
O(23)-Mo(7)-O(22)	86.02(15)	N(5)-Zn(5)-O(42)	96.0(2)
O(5)-Mo(7)-O(22)	156.02(15)	N(3)-Zn(5)-O(42)	93.9(2)
O(6)-Mo(7)-O(22)	82.03(14)	N(4)-Zn(5)-N(6)	97.5(2)
O(38)-Mo(8)-O(33)	105.08(18)	N(5)-Zn(5)-N(6)	78.4(3)
O(38)-Mo(8)-O(22)	103.33(18)	N(3)-Zn(5)-N(6)	174.3(2)
O(33)-Mo(8)-O(22)	97.97(17)	O(42)-Zn(5)-N(6)	86.4(2)
O(38)-Mo(8)-O(3)	102.89(17)	N(4)-Zn(5)-O(19)	93.24(18)
O(33)-Mo(8)-O(3)	148.96(16)	N(5)-Zn(5)-O(19)	149.70(18)
O(22)-Mo(8)-O(3)	88.39(16)	N(3)-Zn(5)-O(19)	87.6(2)
O(38)-Mo(8)-O(1)	100.23(18)	O(42)-Zn(5)-O(19)	55.94(15)
O(33)-Mo(8)-O(1)	88.15(16)	N(6)-Zn(5)-O(19)	87.9(2)

Table S5. Ball and stick representation with partial atomic labeling scheme, selected bond distances (Å) and bond valence calculation (BVC) of the POM unit in **1**.

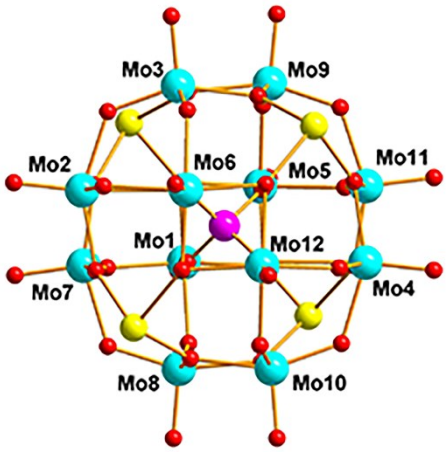


Mo1	O20	1.653	BVS = 6.19	Mo4	O16	1.657	BVS = 4.98
	O8	1.826			O1	1.927	
	O7	1.829			O2	1.955	
	O10	2.000			O7	2.019	
	O10#1	1.994			O13	2.051	
	O6	2.604			O6	2.555	
Mo2	O15	1.645	BVS = 5.05	Mo5	O19	1.682	BVS = 4.95
	O2	1.965			O14	1.962	
	O14#1	1.972			O4	1.968	
	O1	1.974			O3	1.977	
	O12	2.019			O9#1	1.999	
	O5	2.579			O5	2.504	
Mo3	O17	1.677	BVS = 4.92	Mo6	O18	1.684	BVS = 6.12
	O4	1.944			O12	1.825	
	O3	1.961			O9	1.850	
	O8	1.990			O11	2.003	
	O13	2.045			O11#1	2.013	
	O6	2.503			O5	1.967	

The calculated value of average oxidation state of Mo: 5.37

The theoretical value of average oxidation state of Mo: 5.33

Table S6. Ball and stick representation with partial atomic labeling scheme, selected bond distances (Å) and bond valence calculation (BVC) of the POM unit in **2**.



Mo1	O36	1.687	BVS = 4.88	Mo7	O31	1.685	BVS = 4.86
	O23	1.945			O23	1.946	
	O13	1.973			O5	1.970	
	O4	1.975			O6	1.986	
	O33	2.042			O22	2.042	
	O34	2.494			O34	2.525	
Mo2	O37	1.679	BVS = 5.15	Mo8	O38	1.694	BVS = 5.96
	O6	1.964			O33	1.820	
	O5	1.965			O22	1.821	
	O14	2.007			O3	1.997	
	O9	2.075			O1	2.031	
	O7	2.521			O34	2.594	
Mo3	O20	1.702	BVS = 5.98	Mo9	O24	1.689	BVS = 5.93
	O25	1.825			O27	1.828	
	O14	1.827			O16	1.846	
	O17	1.969			O17	1.993	
	O8	2.027			O8	2.015	
	O7	2.541			O11	2.570	
Mo4	O28	1.678	BVS = 4.88	Mo10	O21	1.699	BVS = 6.01
	O32	1.933			O29	1.811	
	O10	1.986			O41	1.820	
	O2	1.987			O3	2.000	
	O29	2.048			O1	2.005	
	O26	2.510			O26	2.604	
Mo5	O18	1.675	BVS = 5.15	Mo11	O39	1.668	BVS = 5.19
	O13	1.948			O2	1.957	
	O4	1.960			O10	1.971	
	O16	2.034			O27	1.998	
	O30	2.108			O30	2.100	
	O11	2.452			O11	2.522	

Mo6	O40	1.676	BVS = 5.15	Mo12	O35	1.672	BVS = 4.91
	O12	1.952			O32	1.955	
	O15	1.967			O15	1.976	
	O25	2.022			O12	1.983	
	O9	2.080			O41	2.029	
	O7	2.526			O26	2.547	

The calculated value of average oxidation state of Mo: 5.34

The theoretical value of average oxidation state of Mo: 5.33

Table S7. The comparison of nonlinear optical properties of compounds **1**-**2** based on Zn-*ε*-Keggin and other POM-based inorganic-organic hybrid materials

Materials	β[a] (cm·GW^{-1})	σ[b] (GM)	Ref.
Compound **1**	0.00419	1819	This work
Compound **2**	0.00240	1127	This work
$[Ni(en)(H_2O)_3][Ni_6(H_2O)_3(en)_2L(\mu_3\text{-}OH)_3(HSiW_9O_{34})]_2\cdot 9H_2O$	0.035	1552	[1]
$[Co(H_2O)_2(DAPSC)]_3\{[Co(H_2O)(DAPSC)]_2BW_{12}O_{40}\}BW_{12}O_{40}\cdot 10H_2O$	0.003553	1522	[2]
$[Mn(H_2O)_2(DAPSC)]_2\{[Na_3(H_2O)_2Mn_{0.5}(H_2O)_4][Mn(H_2O)(DAPSC)]_2[H_3P_5W_{30}O_{110}]\}\cdot 7.5H_2O$	0.002099	888	[3]
$[Co(H_2O)_2(DAPSC)]\{[Co(H_2O)_2(DAPSC)][Na_{1.5}(H_2O)_2]\}\{[Na_{0.5}(H_2O)_2Co_{0.5}(H_2O)_4][Co(H_2O)(DAPSC)]_2[H_4P_5W_{30}O_{110}]\}\cdot 6H_2O$	0.001715	707	[3]
$[(L\text{-}C_4O_6H_2)_2V_4O_8]\cdot 2C_6N_2H_{18}$	0.003167	1412	[4]
$[(D\text{-}C_4O_6H_2)_2V_4O_8]\cdot 2C_6N_2H_{18}$	0.003167	1094	[4]
$[Ni(NTB^c)(H_2O)]_2(H_2P_2Mo_5O_{23})\cdot 9.25H_2O$	0.001655	758	[5]
$[Ni(H_2O)(NTB)]_2(PMo^{VI}_{11}Mo^{V}O_{40})\cdot 4.5H_2O$	0.001127	404	[5]
$[Ni(NTB)]_2(Mo_8O_{26})\cdot 9H_2O$	0.015925	673	[5]
$[Sm(H_2O)_2(DAPSC^d)]_2[Sm(H_2O)_3(DAPSC)]_2[(SiW_{12}O_{40})]_3\cdot 15H_2O$	0.021047	1383	[6]
$[Eu(H_2O)_2(DAPSC)]_2[Eu(H_2O)_3(DAPSC)]_2[(SiW_{12}O_{40})]_3\cdot 15H_2O$	0.013874	669	[6]
$[Tb(H_2O)_2(DAPSC)]_2[Tb(H_2O)_3(DAPSC)]_2[(SiW_{12}O_{40})]_3\cdot 15H_2O$	0.011443	712	[6]
$[C_5NH_5]_8[C_3H_5N_2]_2\{[C_5NH_5]_9[H_{31}Mo_{12}O_{24}Co_{12}(PO_4)_{23}(H_2O)_4]\}\cdot 12H_2O$	0.00263	1058	[7]
$[Co(H_2O)_6]\{[C_3H_4N_2]_2[C_5NH_5]_{14}[H_{15}(Mo_2$	0.01375	622	[8]

$O_4)_8Co_{16}(PO_4)_{14}(HPO_3)_{10}(OH)_3]\}\cdot 5H_2O$			
$[C_3H_5N_2]_4[C_5NH_5]_2[Ni(H_2O)_6]\{[C_3H_4N_2]_2[C$			
$_5NH_5]_{14}[H_{18}(Mo_2O_4)_8N_{i16}(PO_4)_{22}(OH)_6]\}\cdot 1$	0.0056	247	[8]
$1H_2O$			

[a] the TPA absorption coefficient.

[b] the TPA cross-section.

[c] NTB = tris(2-benzimidazyl-methyl)amine

[d] DAPSC = 2,6-diacetylpyridine bis(semicarbazone)

Reference

[1] X. M. Luo, L. Chen, Y. Y. Dong, J. Li, C. H. Cui, J. P. Cao and Y. Xu, *Dalton Trans.*, 2018, **47**, 9504-9511.

[2] G. H. Hu, H. Miao, H. Mei, S. Zhou and Y. Xu, *Dalton Trans.*, 2016, **45**, 7947-7951.

[3] J. Shi, Y. Xiong, M. J. Zhou, L. Chen and Y. Xu, *Rsc Adv*., 2017, **7**, 55427-55433.

[4] J. P. Cao, Y. Xiong, X. M. Luo, L. Chen, J. Shi, M. J. Zhou and Y. Xu, *Dalton Trans.*, 2018, **47**, 6054-6058.

[5] Y. Y. Dong, X. Xu, G. P. Zhou, H. Miao, G. H. Hua and Y. Xu, *Dalton Trans.*, 2015, **44**, 18347-18353.

[6] X. M. Luo, N. F. Li, Z. B. Hu, J. P. Cao, C. H. Cui, Q. F. Lin and Y. Xu, *Inorg. Chem.*, 2019, **58**, 2463-2470.

[7] Y. Y. Dong, G. H. Hu, H. Miao, X. X. He, M. Fang and Y. Xu, *Inorg. Chem.*, 2016, **55**, 11621-11625.

[8] H. Miao, H. X. Wan, M. Liu, Y. Zhang, X. Xu, W. W. Ju, D. R. Zhua and Y. Xu, *J. Mater. Chem. C*, 2014, **2**, 6554-6560.