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Supporting information for article:

Two new POM-based compounds modified by lanthanide–Schiff base complexes with interesting NLO properties

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Two new POMs-based compounds modified by lanthanide Schiff base complexes with interesting NLO properties

S1. The third-order nonlinear optics

The electronic spectra of compounds **1 - 2** in DMF at a concentration of 1.0×10^{-4} mol·L^{-1} give the nonliner absorption at room temperature. Two-photon absorption (TPA) values containing TPA coefficient β and TPA cross section σ were measured by the open-aperture Z-scan technique with femtosecond laser pulse and Ti:95 sapphire system. Figures 5 and 6 show the open aperture Z-scan curves of compound **1-2**. The black dots are the experimental data, and the red lines represent the theoretical simulated curves modified by the following equations (eqn (1) and (2)):

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

$$q_0(z) = \frac{\beta I_0 L_{eff}}{1 + z^2 / z_0^2} \tag{2}$$

where β is the TPA coefficient of the solution, I_0 is the input intensity of laser beam at the focus $z = 0$, $L_{eff} = (1-e^{-\alpha L})/\alpha$ is the effective length with α and L are the linear absorption coefficient and the sample length respectively. Z is the sample position, $z_0 = \pi \omega_0^2 / \lambda$ is the diffraction length of the beam, in which the ω_0 and λ are the spot size at the focus and the wavelength of the beam respectively. Furthermore, the molecular TPA cross section σ can be calculated by the following relationship:

$$\sigma N_A d \times 10^{-3} = h\nu\beta \tag{3}$$

where N_A, d, h and v are respectively the Avogadro's constant, the concentration of the compound, the Planck's constant and the frequency of input intensity.

Table S1   The third-order NLO data of complexes **1 – 2**.

Compounds	β[a] (cm·GM^{-1})	σ[b] (GM[c])	λ (nm)
1	0.05352	2264	700
2	0.30330	941	820

[a] the TPA absorption coefficient of the solution.

[b] the molecular TPA cross-section.

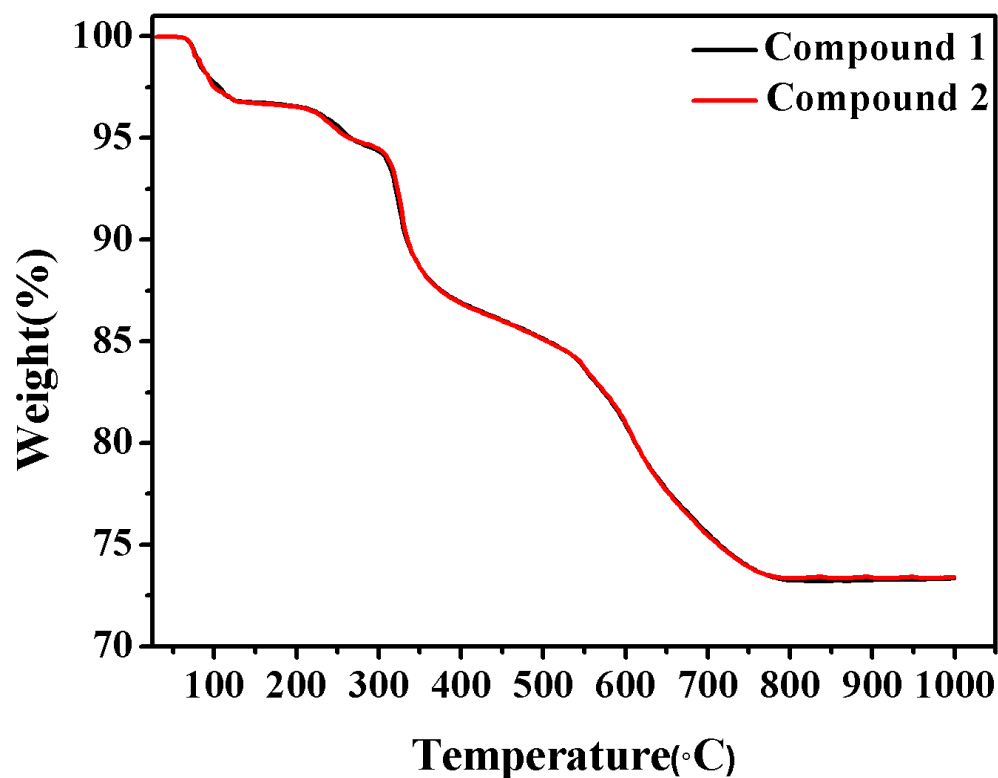[c] 1 GM = 10^{-50} cm^{4}s per photon.

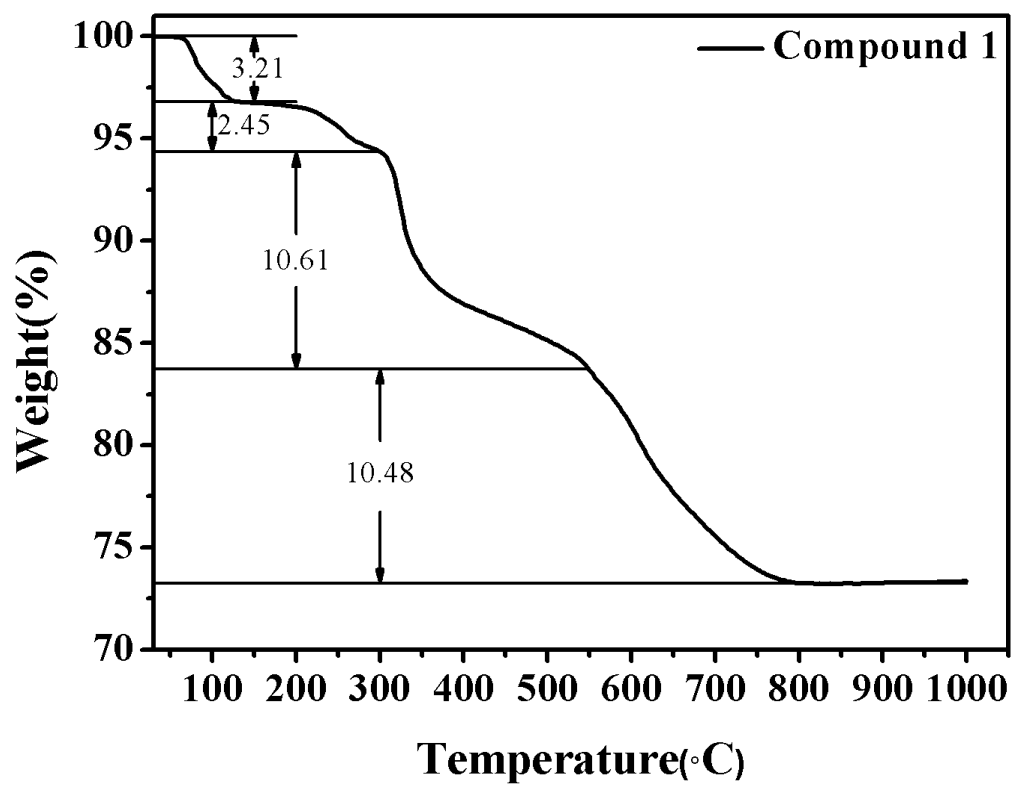**S2. Characterization**

Figure S1 The TGA curve for **1** and **2**.

Figure S2 The TGA curve for **1**.
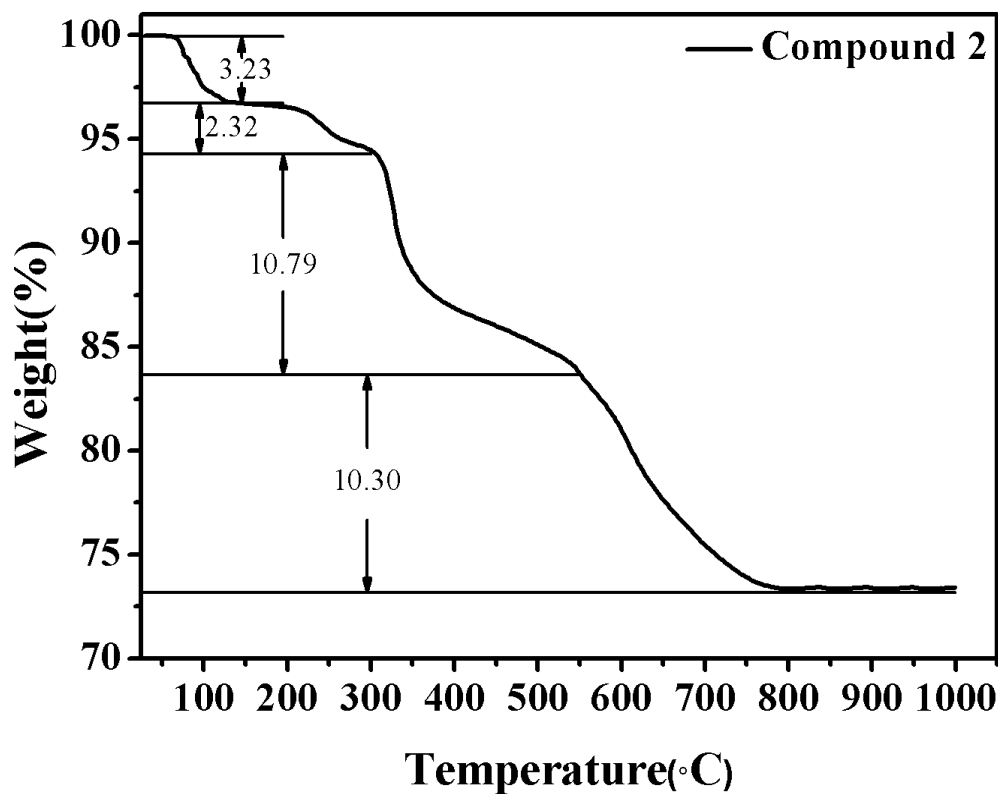
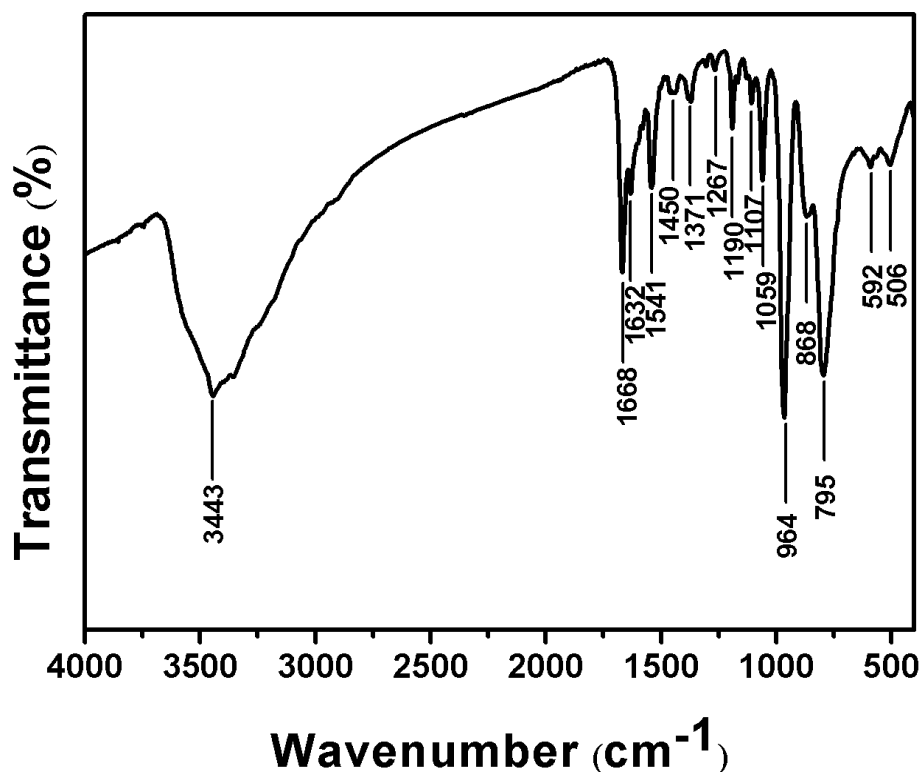**Figure S3** The TGA curve for **2**.

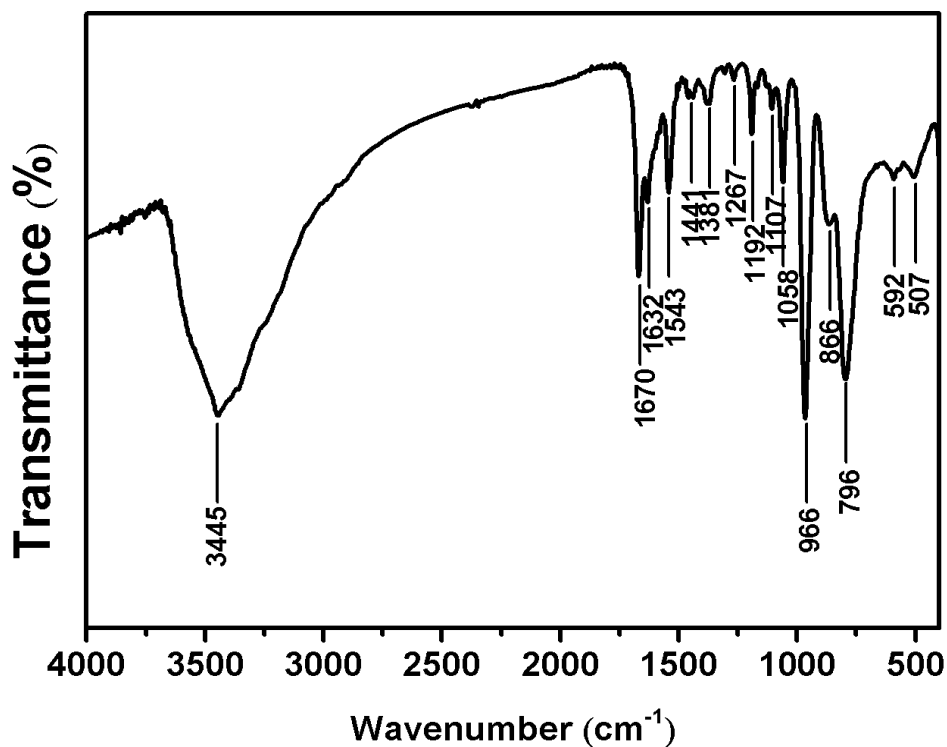**Figure S4** The IR spectrum of **1**.
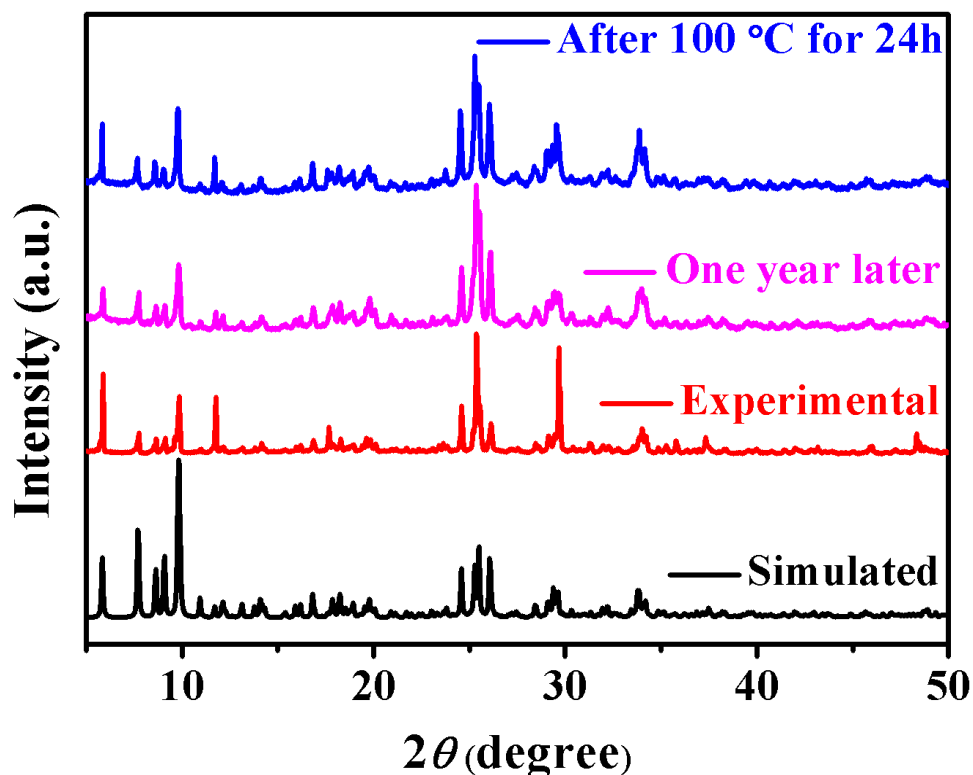
Figure S5 The IR spectrum of **2**.

Figure S6 PXRD patterns of **1** (in ascending order): simulated, experimental, one year later in the sample vial under ambient conditions, and kept for 24 h in the constant temperature (100 °C) of oven.

Figure S7 PXRD patterns of **2** (in ascending order): simulated, experimental, one year later in the sample vial under ambient conditions, and kept for 24 h in the constant temperature (100 °C) of oven.
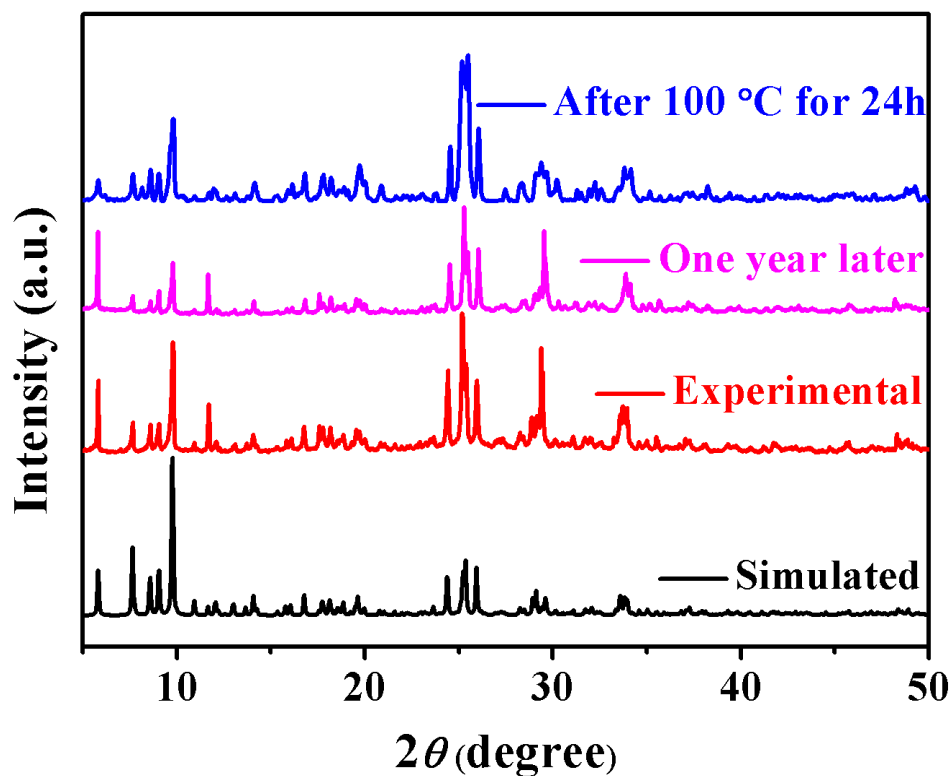
S3. Electrochemical properties

Table S2   The mean peak potentials $E_{1/2}$ of **1-CPE**, **2-CPE** and **3-CPE**.

CPE	The mean peak potentials $E_{1/2}$ (mV, 200 mV s^{-1})			
	I-I'	II-II'	III-III'	IV-IV'
1-CPE	440	257	41	-134
2-CPE	446	253	55	-120
3-CPE	414	281	43	-122