Electronic Supplementary Information

One-dimensional and two-dimensional coordinationpolymers from cluster modular construction

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Experiment section

1. General procedures

Elemental analyses (C, H and N) were measured on a Carlo-Erba CHNO-S microanalyzer. UV−Vis spectra of solution and solid state were performed by Varian Cary-50 UV−Vis spectrophotometer. Fourier-transform infrared (FT-IR) spectra in the range 4000-400cm^{-1} were conducted by Varian 1000 FT-IR spectrometer as KBr disks. ESI-TOF MS spectra were recorded on a Bruker micrOTOF-Q III mass spectrometer. Thermogravimetric analysis (TGA) was conducted by Mettler Toledo Star System at a heating rate of 10 °C/min under nitrogen atmosphere.

2. Third-order NLO measurement and details of 1-3

The solutions of **L1** and **1-3 (**5.02 × 10^{-4} M) in MeCN were placed in a 2 mm quartz cuvette. They were stable in air and laser irradiation under experimental conditions. The pico-second *Z*-scan technique and a linear polarized laser light (λ = 532 nm; repetition rate = 2 Hz; width = 15 ps) generated from a frequency-doubled, mode-locked, Q-switched Nd: YAG laser were applied to investigate absorption and refraction. The test method was the same as that reported previously.[S1]

The nonlinear absorption data of **1-3** in MeCN were measured using the *Z*–scan technique with open aperture. The transmittance of light (*T*) is a function of the sample's *Z* position. The nonlinear absorption ($\alpha = \beta(I_i)$) and the linear absorption coefficient (α_0) are determined by formula (**1**) below:

$$T(Z) = \frac{\alpha_0}{\sqrt{\pi}\beta I_i(Z)(1-e^{-\alpha_0 L})}\int_{-\infty}^{\infty}\ln\left[1+\beta I_i(Z)\frac{1-e^{-\alpha_0 L}}{\alpha_0}e^{-\tau^2}\right]d\tau \quad (\mathbf{1})$$

where α is the effective third-order NLO absorptive coefficient, τ is the time, and *L* was the sample thickness.

The nonlinear refractive data was determined by the ratio of the transmittance measured by closed- and open-aperture. The difference between trough and peak positions ($\Delta Z_{V\text{-}P}$), and difference between their normalized transmittance values ($\Delta T_{V\text{-}P}$) fit the following two formula originated for a third-order NLO process. Also, the effective third-order NLO refractive index n_2 could be achieved by calculation with formula (**3**):

$$\Delta Z_{V-P} = 1.72\pi\omega_0^2/\lambda \quad (\mathbf{2})$$

$$n_2^{eff} = \lambda\alpha_0\Delta T_{V-P}/\left[0.812\pi I\left(1-e^{\alpha L}\right)\right] \quad (\mathbf{3})$$

where *I* is the peak irradiation intensity at focus, and λ is the wavelength of the laser.[S2]

The effective third-order NLO susceptibility $\chi^{(3)}$ and the second hyperpolarizability γ values could be obtained by calculation with the following formulae (**4**)–(**7**) from β and n_2.

$$\chi_I^{(3)} = 9 \times 10^8 \varepsilon_0 n_0^{\ 2} c^2 \beta/(4\omega\pi) \quad (\mathbf{4})$$

$$\chi_R^{(3)} = c n_0^{\ 2} n_2/(80\pi) \quad (\mathbf{5})$$

$$\chi^{(3)} = [(\chi_I^{(3)})^2 + (\chi_R^{(3)})^2]^{1/2} \quad (\mathbf{6})$$

$$\gamma = \chi^{(3)}/[N((n_0^{\ 2} + 2)/3)^4] \quad (\mathbf{7})$$

Where N is the density of the molecules in the unit of number of molecules per cubic centimeters, and n_0 is the linear refractive index of MeCN (n_0 = 1.34),c is the speed of light, and ω is the optical frequency.

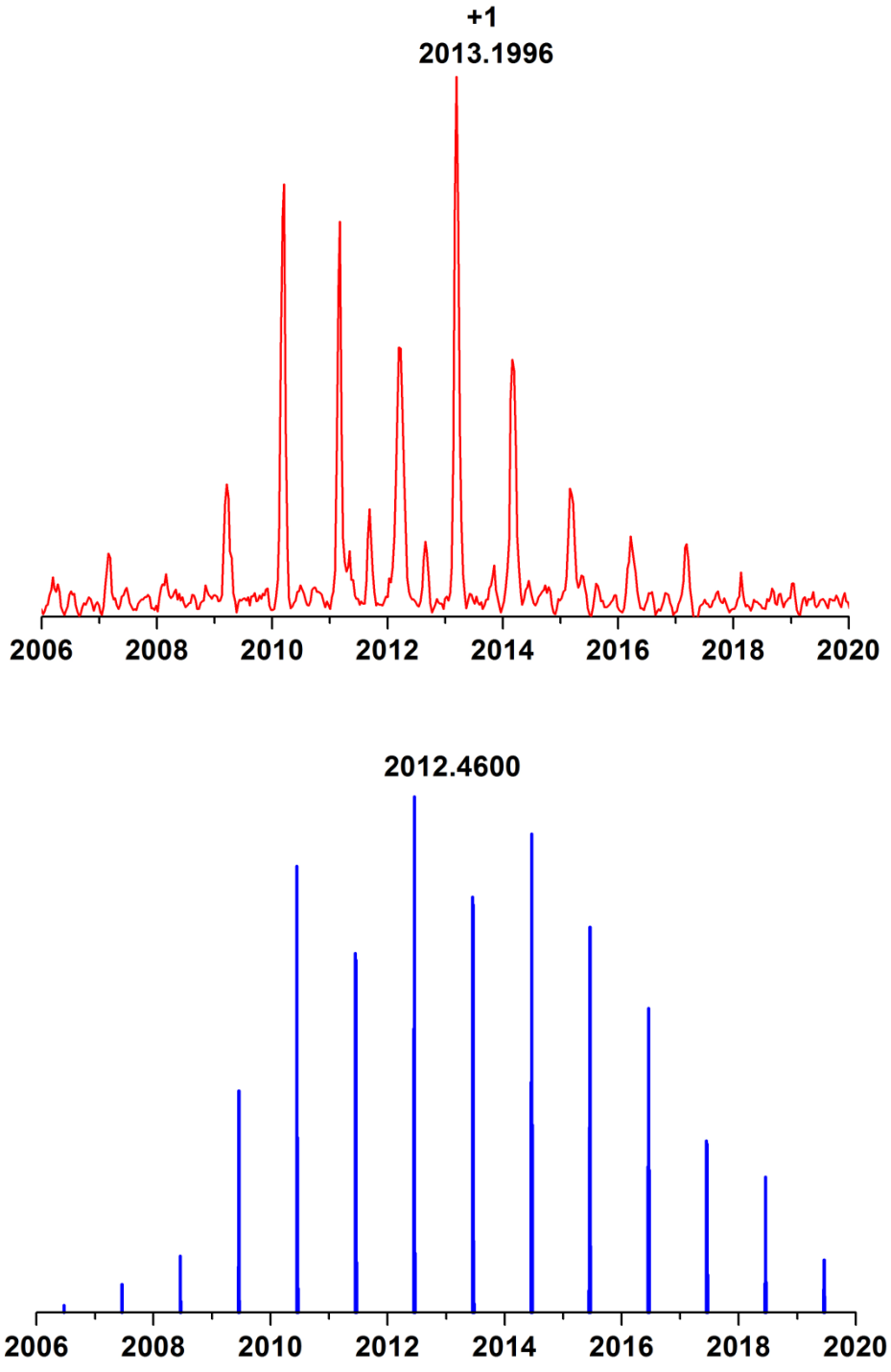

Fig. S1 Experimental (top) and theoretical (bottom) ESI-TOF-MS spectra of $[Tp^*WS_3Cu(\mathbf{L1})_2 + 2CH_3OH + H]^+$ in **2**.

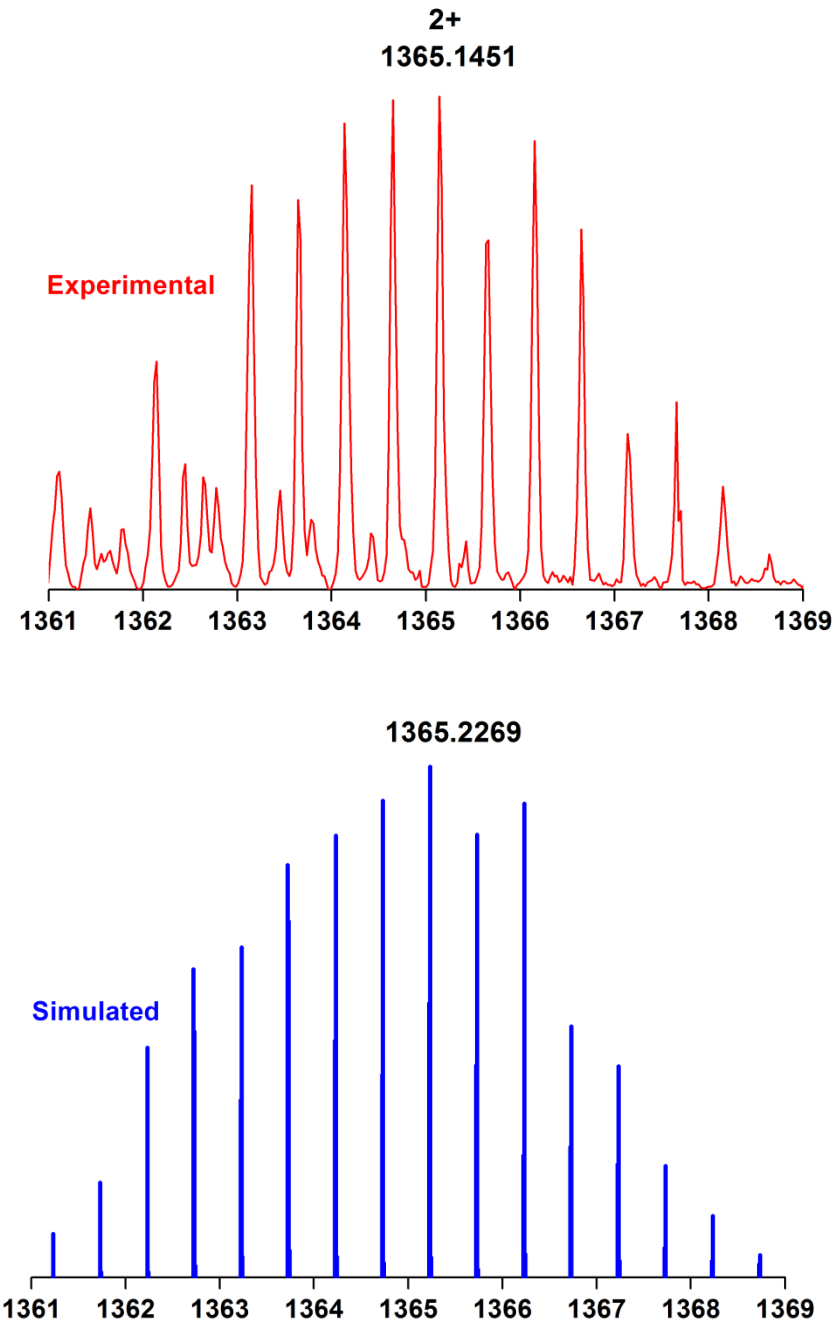

Fig. S2 Experimental (top) and theoretical (bottom) ESI-TOF-MS spectra of $[Tp^*WS_3Cu_3(\mathbf{L1})_3]^{2+}$ in **3**.

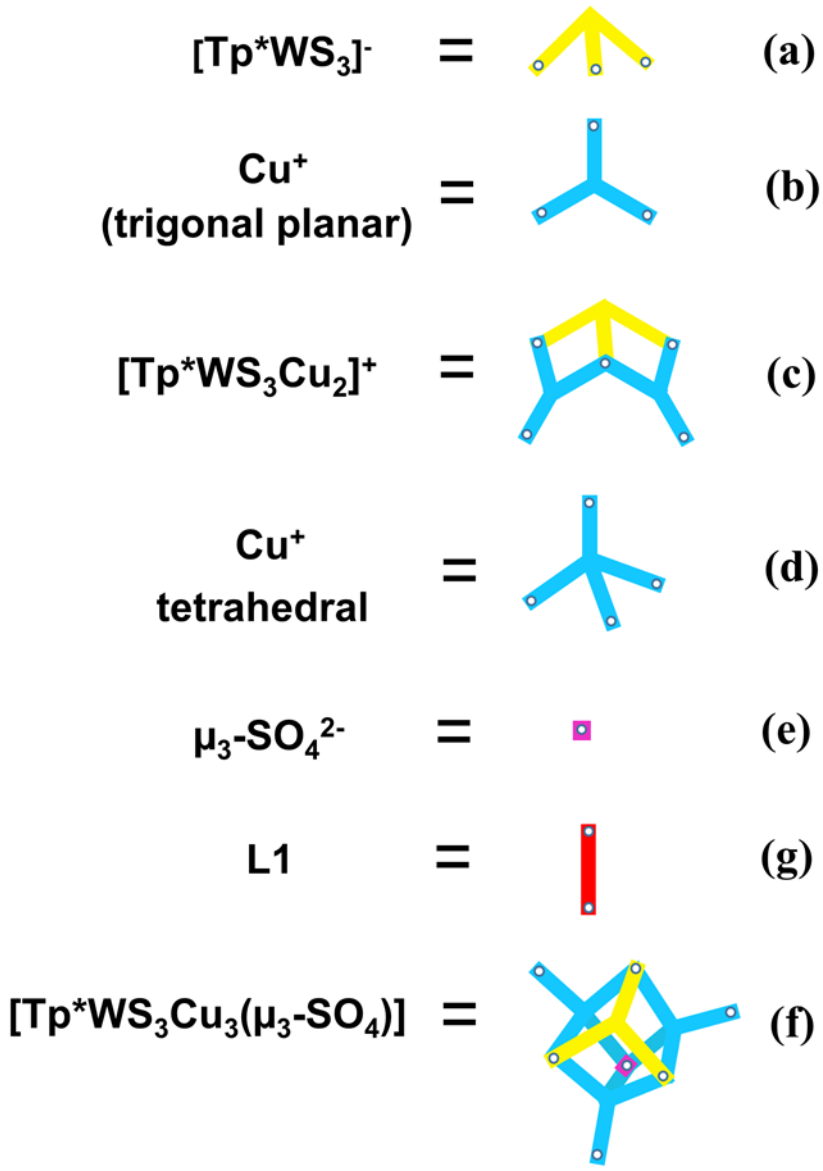

Fig. S3 Modules for the basic structural components of **2** and **3**.

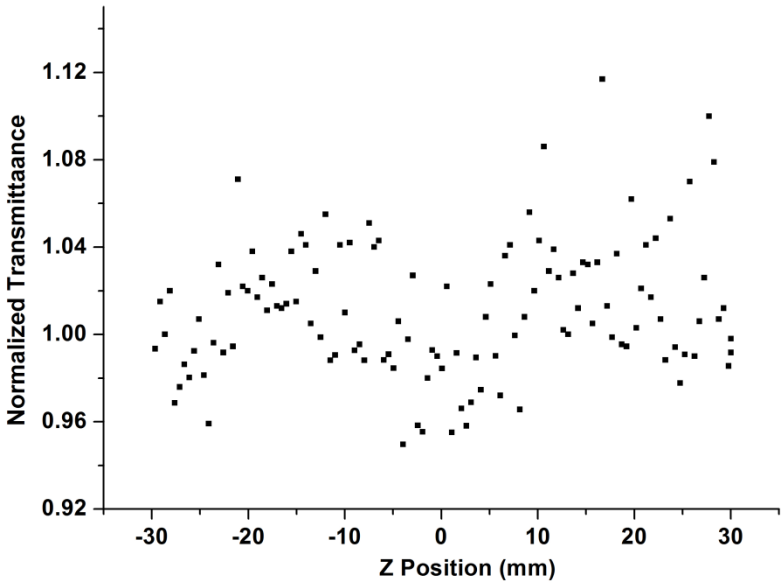

Fig. S4 Normalized *Z*-scan data of **L1** (5.02×10^{-4} M in MeCN at 532 nm) under open-aperture conditions, showing no detectable nonlinear absorption signal.

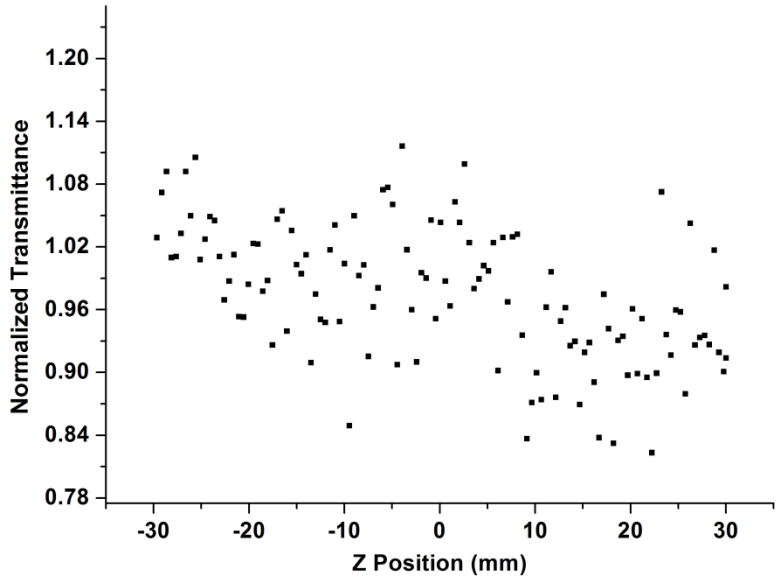

Fig. S5 Normalized *Z*-scan data of **L1** (5.02×10^{-4} M in MeCN at 532 nm) under closed-aperture conditions, showing no detectable nonlinear refraction signal.

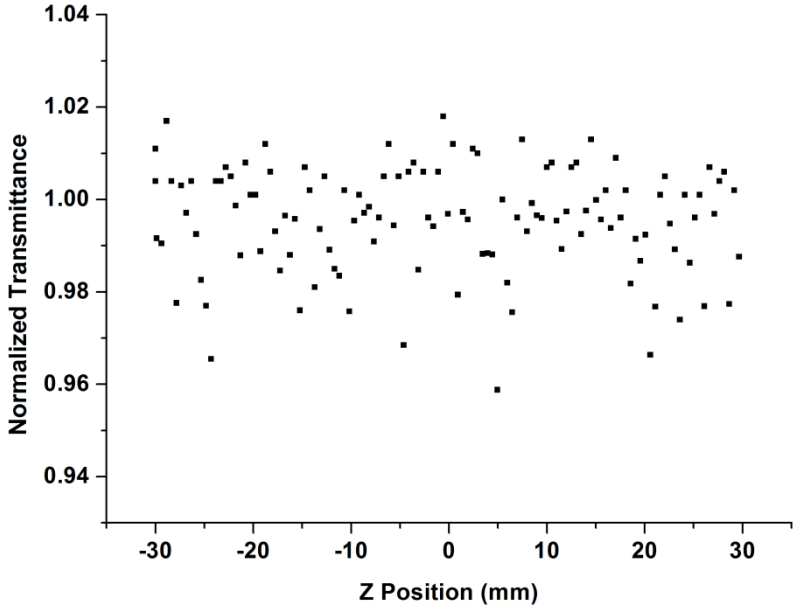

Fig. S6 Normalized *Z*-scan data of **1** (5.02×10^{-4} M in MeCN at 532 nm) under open-aperture conditions, showing no detectable nonlinear absorption signal.

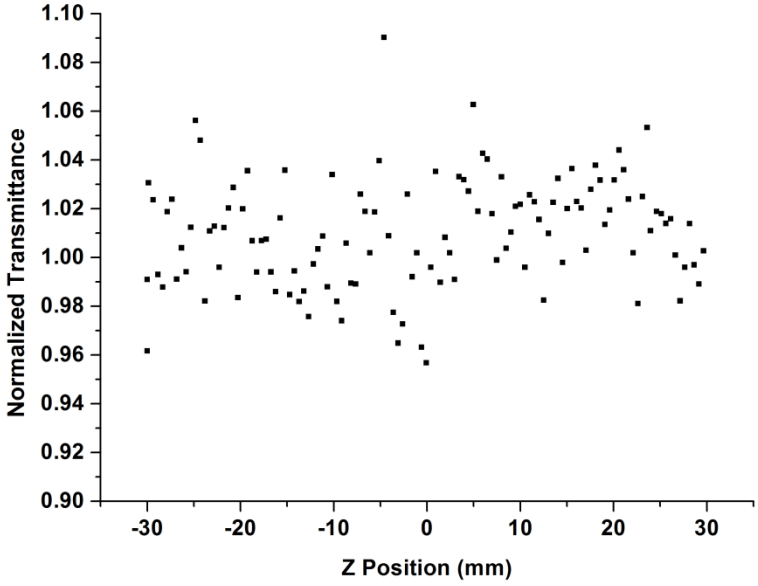

Fig. S7 Normalized *Z*-scan data of **1** (5.02×10^{-4} M in MeCN at 532 nm) under closed-aperture conditions, showing no detectable nonlinear refraction signal.

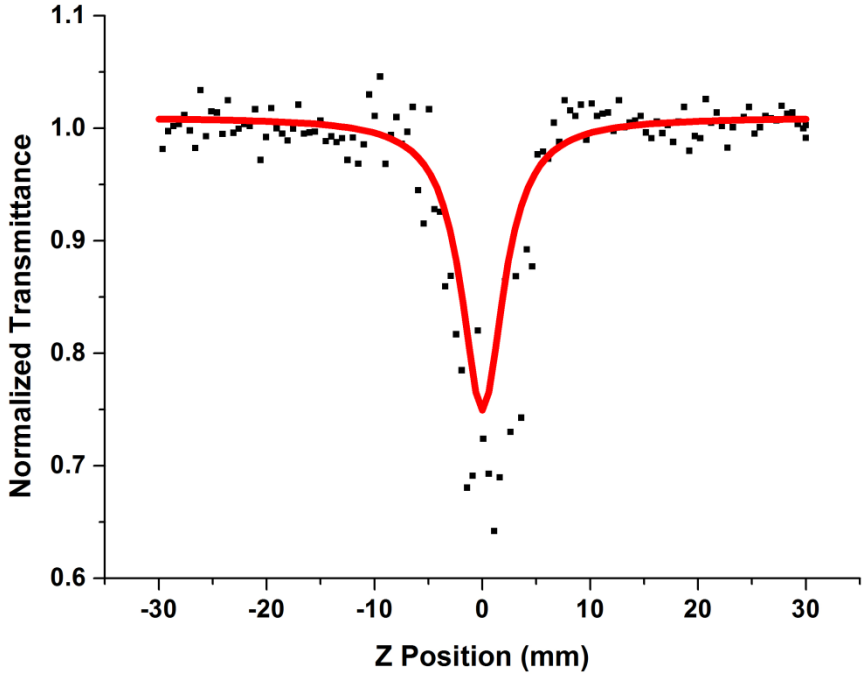

Fig. S8 Normalized *Z*-scan data of **2** (5.02×10^{-4} M in MeCN at 532 nm) under open-aperture conditions, showing the nonlinear absorption.

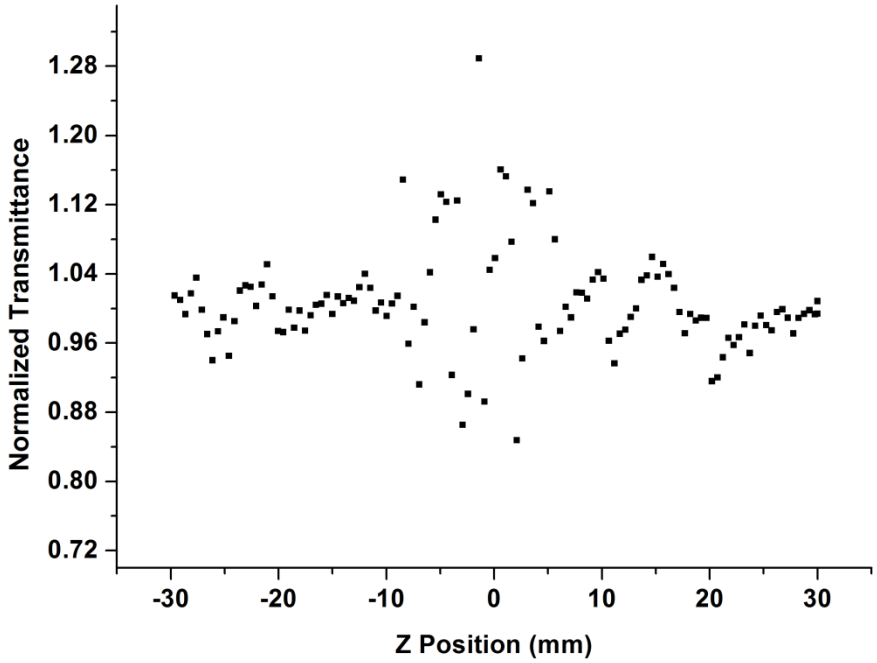

Fig. S9 Normalized *Z*-scan data of **2** (5.02×10^{-4} M in MeCN at 532 nm) under closed-aperture conditions, showing no detectable nonlinear refraction signal.

Table S1 The third-order NLO parameters for **2** and **3**.

Compound	T_0	n_2 (10^{-17}esu)	$\chi_R^{(3)}$ (10^{-11}esu)	$\chi_I^{(3)}$ (10^{-11} esu)	$\chi^{(3)}$ (10^{-11}esu)	γ (10^{-29}esu)
2	65%	/	/	0.27	0.27	0.36
3	49%	-2.0	-4.29	0.23	4.30	5.57

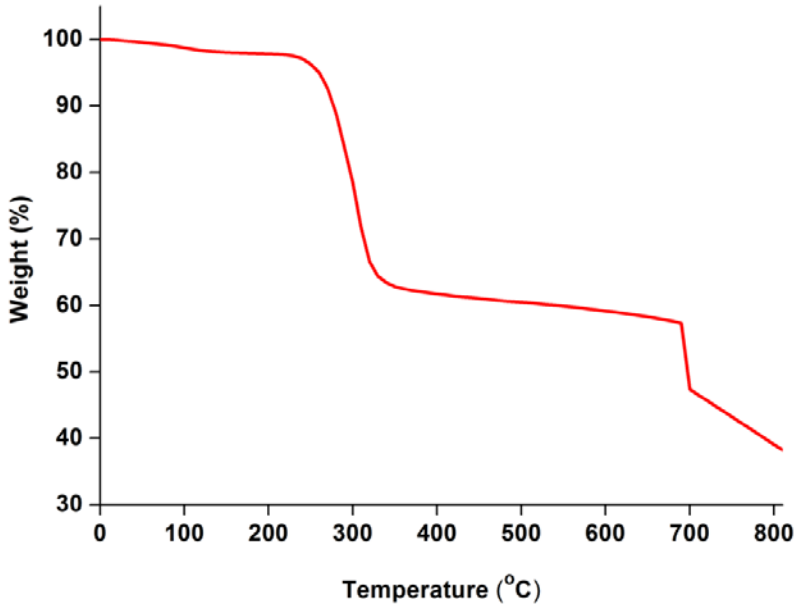

Fig. S10 The TGA curve of **2**.

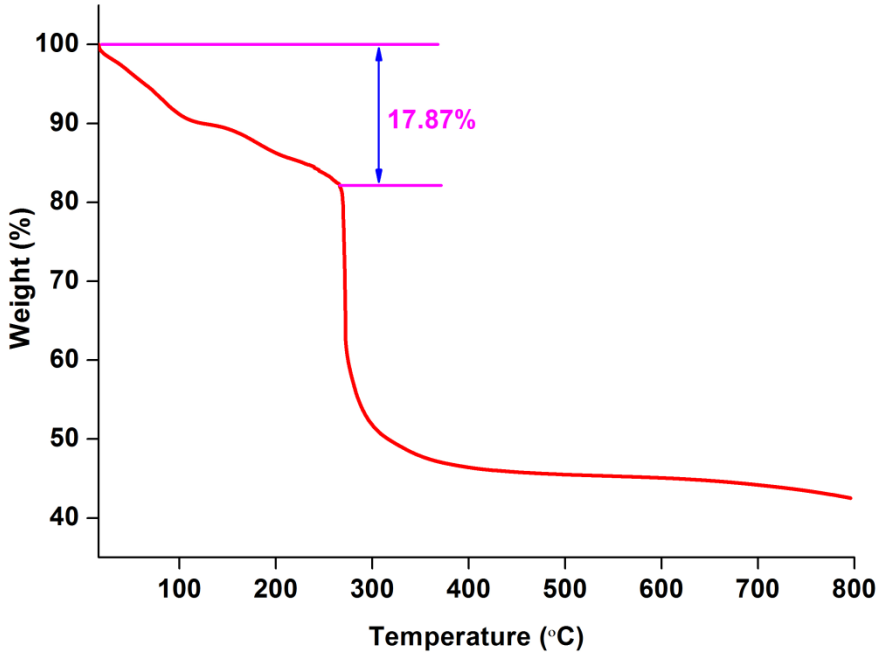

Fig. S11 The TGA curve of **3**.

According to the TGA data, about ten Et_2O molecules were calculated by weight loss before 265 °C for **3** (obsd: 17.87%, calcd: 18.00%).

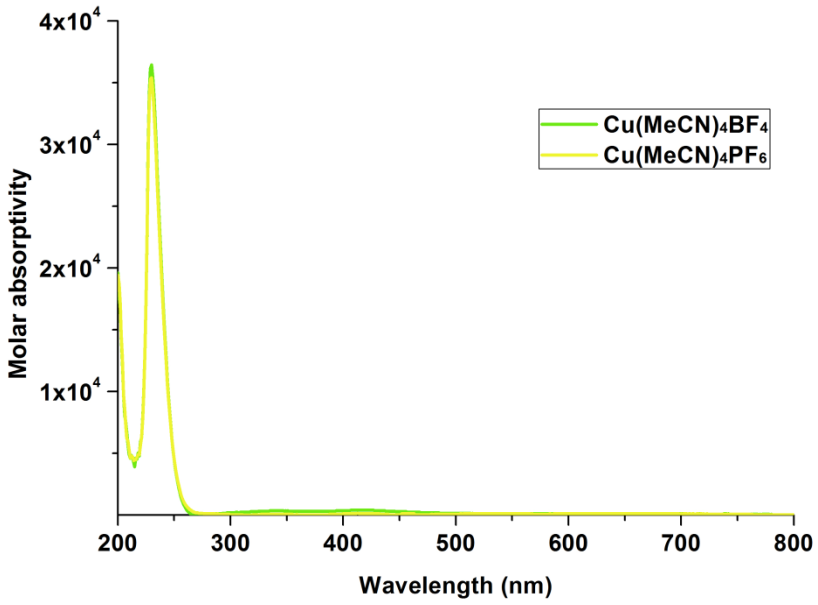

Fig. S12 UV-vis spectra of $Cu(MeCN)_4BF_4$ and $Cu(MeCN)_4PF_6$ (2.50×10^{-5} M) in MeCN.

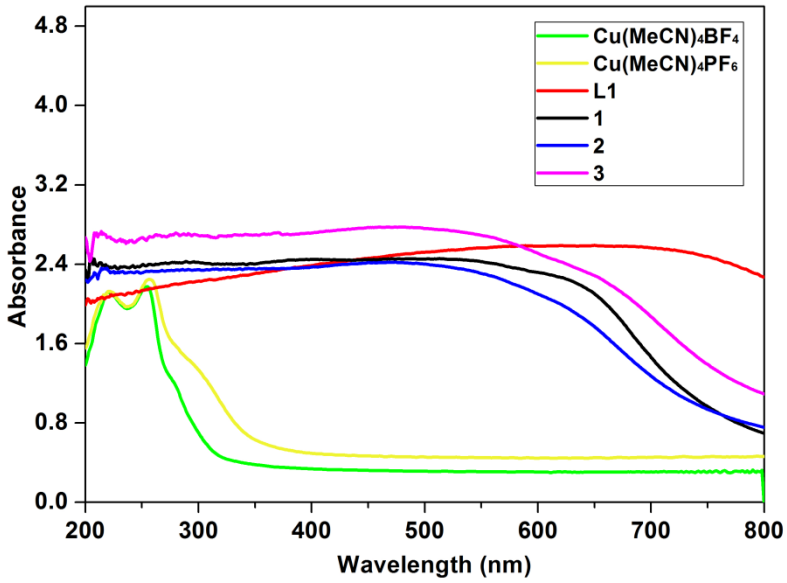

Fig. S13 UV-vis spectra of **L1**, **1**, **2**, **3**, $Cu(MeCN)_4BF_4$ and $Cu(MeCN)_4PF_6$ measured in the solid state.

References

S1. Z. G. Ren, H. X Li, L. L. Li, Y. Zhang, J. P. Lang, J. Y. Yang and Y. L. Song, *J. Organomet. Chem.*, 2007, **692**,2205–2215.

S2. M. Sheik-Bahae, A. A.Said, T. H. Wei, D. J.Hagan and E. W. Van Stryland, *Quantum Electron.*, 1990, **26**, 760–769.