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Supplementary Information

Nonlinear optical properties of a one-dimensional coordination polymer

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S1. Supplementary Figures

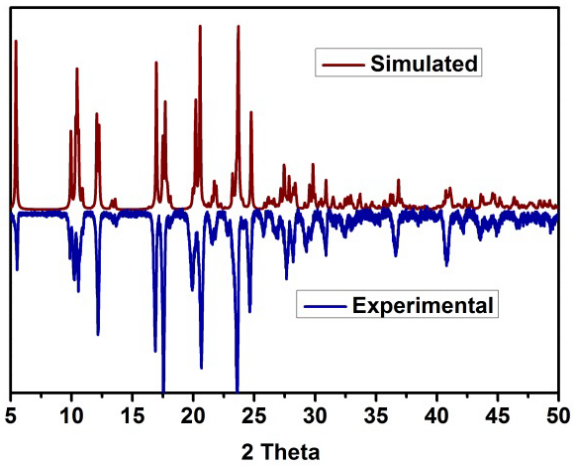

Figure S1: Simulated and bulk PXRD patterns of **1**.

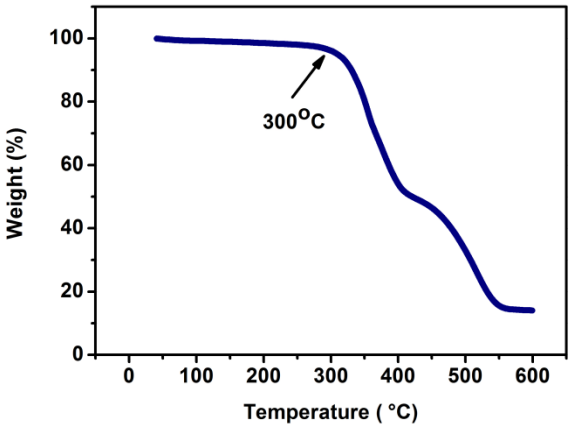

Figure S2: TGA of **1**. The compound is stable up to 300°C.

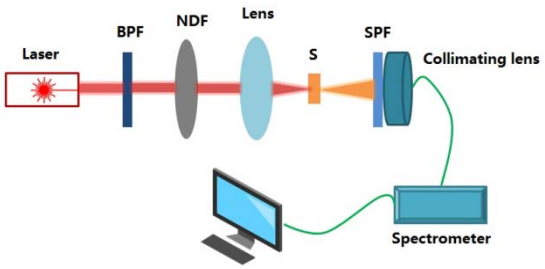

Figure S3: Experimental setup for multi-photon-excited PL, SHG and THG measurements.The excitation wavelength was 800 nm, or varied between 1100 nm and 1500 nm. BPF: band pass filter; NDF: neutral density filter; S: sample; and SPF: short pass filter.

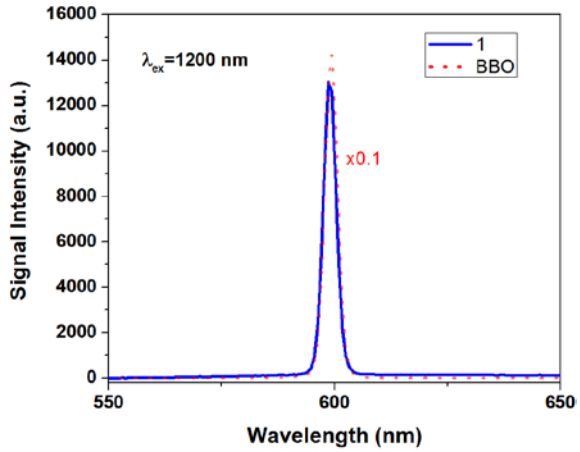

Figure S4: SHG from **1** and BBO excited at 1200 nm.

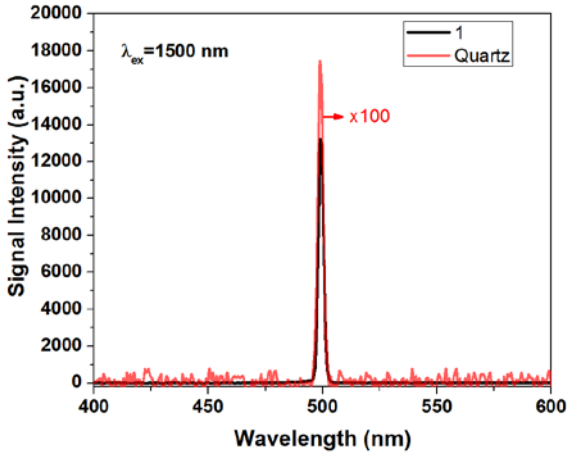

Figure S5: THG from **1** and α-quartzexcited at 1500 nm.

S2. Supplementary Tables

Compound	**1**
Formula	C84 H60 N4 O8 Zn2
Formula weight	1384.1
Crystal system	Triclinic
Space Group	*P*ī
a, Å	10.3376(6)
b, Å	10.4327(6)
c, Å	17.2410(12)
α/°	72.432(2)
β/°	88.856(3)
γ/°	60.397(2)
V, $Å^3$	1522.49(17)
Z	2
$\rho_{cal,}$ Mg/m^3	1.51
μ, mm^{-1}	0.858
T	100(2) K
R1	0.0759
wR2	0.0988
GOF	1.022

Table S1: Crystal cells data

S3. Supplementary Text

Synthesis and solid structure.

All the chemicals and solvents were of reagent or better grade and purchased from different commercial resources and used without further purification. An2Py was synthesized according to a reported procedure[1-3]. Powder X-ray diffraction (PXRD) data were recorded on a D5005 Siemens X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.54056 Å) at room temperature (298 K). Thermal Gravimetric Analysis of **1** was obtained using Discovery TGA TA instrument under nitrogen gas flow with a heating rate of 5˚C min^{-1}, and analysis was performed with Trios V3.1. The C, H, and N analyses were carried out using ElementarVarioMicro Cube instrument at the Elemental Analysis Lab, CMMAC, Department of Chemistry, National University of Singapore.

Preparation of the An2Py ligand can be found in Ref. [1-3].

The one-dimensional (1D) CP, $[Zn_2(benzoate)_4(An2Py)_2]$, investigated here was obtained as orange rectangular single crystals from $Zn(NO_3)_2.6H_2O$, An2Py, and sodium benzoate by a layering method using a mixture of methanol, tetrahydrofuran, acetonitrile and water in 52% yield. $Zn(NO_3)_2.6H_2O$ (2.98 mg, 0.01 mmol) in 0.20 mL of methanol was layered over An2Py (3.84 mg, 0.01 mmol) in 0.5 mL of THF and sodium benzoate (2.88 mg, 0.02 mmol) in 0.2 mL water with acetonitrile as middle buffer layer. Several orange plate-like crystals were obtained and washed with THF. Yield: 52%. Elemental analysis (%) Calcd for C-72.89, H-4.31, N-4.05- Found C-68.63, H-4.30, N-4.32.

Multiphoton-excited PL, SHG and THG measurements.

The experimental set-up is schematically described in Fig. S3. The laser pulses (wavelength range: 400−1600 nm; repetition rate, 1 kHz; and pulse width: 150−250 fs) were generated by an optical parametric amplifier (OPA, TOPAS-C, Light-Conversion). The OPA was pumped by a regenerative amplified femtosecond Ti:Sapphire laser system (wavelength, 800 nm; repetition rate, 1 kHz; pulse energy, 3 mJ; and pulse width, <150 fs, Libra, Coherent) which was seeded by a femtosecond Ti:Sapphire oscillator (800 nm, 80 MHz, pulse width <100 fs, Vitesse 800-2, Coherent). The OPA output was filtered by a band pass filter (BPF) to block laser light of undesired wavelengths. The incident energy of the laser pulses was controlled by using a set of neutral density filters (NDFs) and was monitored by an optical power meter (Optical Power Meter 1917-R, Newport) with the detector (Detector 919P-003-10, Newport). PL, SHG and THG signals were collected by a spectrometer (QE Pro, Ocean Optics, resolution of 0.14 nm). A short-pass filter (SPF) was inserted in front of the spectrometer for blocking the transmitted or scattered laser light at excitation wavelengths.

Determination of second-order nonlinearity $|d_{eff}|$

With a measurement similar to the one in Ref. [4], we measured the refractive index of $n_\omega = 2.9$ at1200 nm and $n_{2\omega} = 3.3$ at 600 nm when the probing light propagated along the *c*-axis of **1**. For the1-mm-thick BBO crystal, $n_{\omega\_BBO} \approx 1.54$ at 1200 nm, $n_{2\omega\_BBO} \approx 1.56$ at 600 nm and the second-order nonlinearity, $|d_{BBO}|$ = 2 pm/V.[6]The SHG signal intensity can be expressed as below.[6, 7]

$$I_{2\omega}(L) = \frac{2\omega^2}{c^3 n_\omega^2 n_{2\omega} \varepsilon_0} \left|d_{eff}\right|^2 I_\omega^2 L^2 \frac{sin^2(\frac{\Delta kL}{2})}{(\frac{\Delta kL}{2})^2}$$ Equation S1

where$L$ is the thickness (= 0.04 mm for **1**), $\Delta k = k(2\omega) - 2k(\omega)$ is the difference in the wavenumber; and$I_{2\omega}$and $I_\omega$are the light irradiance at 2ω and ω, respectively.In Fig. S4, we recorded the SHG signals from the single crystal of **1** and the BBO crystal under the same experimental set-up with the same excitation irradiance. From their ratio, we deduced$\left|d_{eff}\right| \approx 3.2|d_{BBO}| \approx 6.4$ pm/V for the single crystal of **1**.

Determination of third-order nonlinearity$\chi^{(3)}$

In Fig. S5, we measured the THG signals from the single crystal of **1** and the 0.5-mm-thick α-quartz sample under the same set-up with the same excitation irradiance. The THG signal intensity can be expressed as below.[6]

$$I_{3\omega}(L) \propto L^2 \left|\chi^{(3)}\right|^2 \frac{sin^2\left(\frac{\Delta kL}{2}\right) + sinh^2(\alpha L/4)}{\left(\frac{\Delta kL}{2}\right)^2 + \left(\frac{\alpha L}{4}\right)^2} e^{-\frac{\alpha L}{2}} I_\omega^3$$ Equation S2

where$L$ is the thickness of **1**(= 0.04 mm), $\Delta k = k(3\omega) - 3k(\omega)$ is the difference in the wavenumber;α is the absorption coefficient at 3ω; and $I_{3\omega}$andI_ω are the light irradiance at 3ω and ω, respectively.For α-quartz, α = 0 cm^{-1} at 533 nm;and $\chi_s^{(3)} = 2.6 \times 10^{-14}\ esu$.[5,8] For the single crystal of 1, we measuredthat$\alpha \approx 400\ cm^{-1}$;$n_\omega = 2.8$, and $n_{3\omega} = 3.4$. From the ratio of THG signal from 1 to THG signal from the α-quartz in Fig. S5, we deduced $\chi^{(3)} = 8 \times 10^{-11}\ esu$for the single crystal of **1**.

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