Supporting Information

Fluorescent and photochromic bifunctional molecular switch based on a stable crystalline metal-viologen complex

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Experimental Section

General: All the reagents were purchased from commercial channels and used without further purification; N-(3-carboxyphenyl)-4,4′-bipyridinium chloride was synthesized as reported.[S1] A TA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N_2 at a rate of 10 ºC min^{-1}. The X-ray powder diffraction (XRD) data were collected with a Bruker D8 Advance X-ray diffractometer using CuKα radiation (λ = 1.5406 Å). UV-Visible spectral measurements were carried out using a HITACHI U-3010 spectrometer. The emission/excitation spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer. IR spectra were characterized by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm^{-1} using a KBr disk. The C, H and N microanalyses were carried out with a Vario EL III elemental analyzer.

Synthesis of [Zn(CPBPY)(HBTC)]·H_2O **1**: $Zn(NO_3)_2·6H_2O$ (59.4mg, 0.2mmol) was added to a mixture of N-(3-carboxyphenyl)-4,4′-bipyridinium chloride (31.2 mg, 0.1mmol), and 1, 3, 5-H_3BTC (42.0mg，0.2mmol) in DMF (5ml), C_2H_5OH (3ml) and H_2O (2ml). The mixture was sealed in a 25ml Teflon-lined steel bomb and heated at 100ºC for 48h. Yellow block-like crystals were collected by filtration, washed by water, and dried at room temperature (0.054mmol, 30.6mg, 54% yield based on N-(3-carboxyphenyl)-4,4′-bipyridinium chloride). Elemental Anal. Calc. (%) for $C_{26}H_{18}N_2O_9Zn$ (567.79): C, 55.00; H, 3.20; N, 4.93. Found: C, 54.55; H, 3.27; N, 4.89.

References:

S1 D. Bongard, M. Möller, S. N. Rao, D. Corr and L. Walder, *Helv. Chim. Acta*, 2005, **88**, 3200.

‡Crystal data for **1**: $C_{26}H_{18}N_2O_9Zn$, fw = 567.79 $g \cdot mol^{-1}$, Monoclinic, space group P21/c, a= 9.5601(19) Å, b= 14.382(3) Å, c= 18.401(5) Å, α = 90º, β = 113.56(2)º, γ = 90º, V = 2318.6(9) $Å^3$, Z = 4, ρ_{calcd} = 1.627 $g \cdot cm^{-3}$, final R1 = 0.0461 and wR2 = 0.1322 for 3245 independent reflections [I＞2σ(I)]. The data were measured on a Rigaku R-AXIS SPIDER CCD diffractometer with MoKα radiation (λ = 0.71073 Å) at 298K. The structure was solved by direct methods and refined by full-matrix leastsquares methods with SHELXL. CCDC 891455 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ukf/data_request/cif.

The calculation of kinetic rate constants:

After irradiation UV-Vis and fluorescent spectra are recorded and the calculations of kinetics of light reversion and fluorescence quenching based on the intensity values of the wavelength at 612 nm (UV-Vis spectra) and 500 nm (fluorescent spectra) respectively. The kinetic rate constants are determined by the literature calculation method.[S2] The following equation is used for data treatment:

$$In\frac{A_\infty - A_0}{A_\infty - A_t} = kt$$

where A_0, A_t, A_∞ are the observed absorption data (612 nm)/ fluorescent emission (500 nm) at the beginning, versus time, and at the end of the reaction, respectively

S2 T. Kawato, H. Koyama, H. Kanatomi and M. Isshiki, *J. Photochem.*, 1985, **28**, 103.

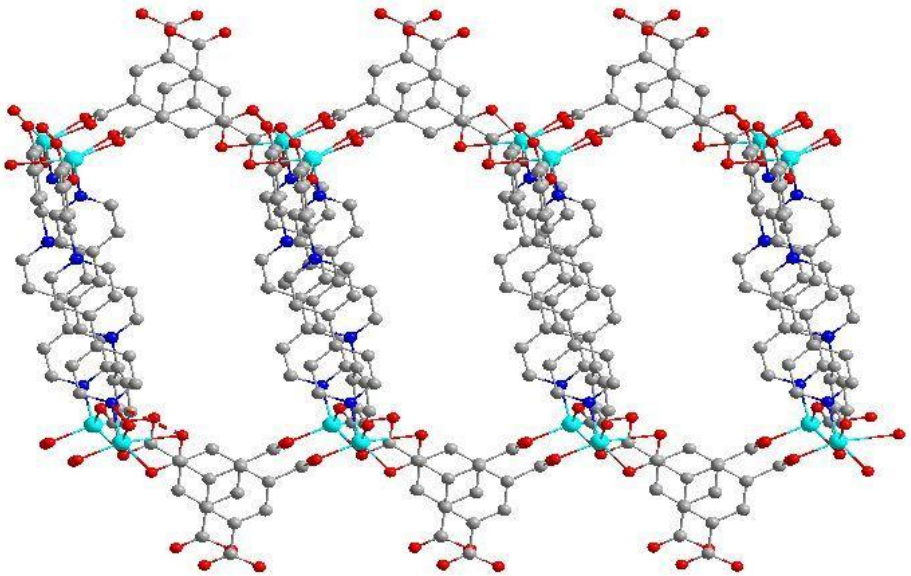

Fig. S1 Views of the 2D layer structure.

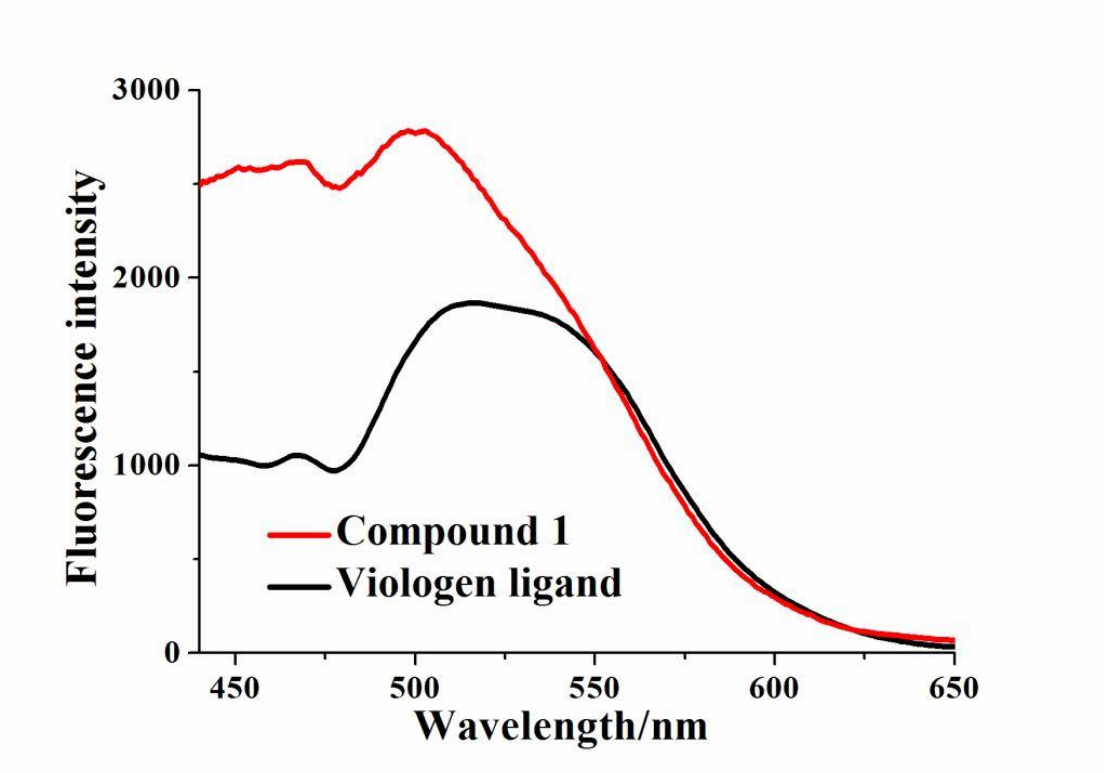

Fig. S2 Fluorescent spectra of compound **1** and the N-(3-carboxyphenyl)-4,4′-bipyridinium (CPBPY) ligand, λ_{EX} = 365 nm.

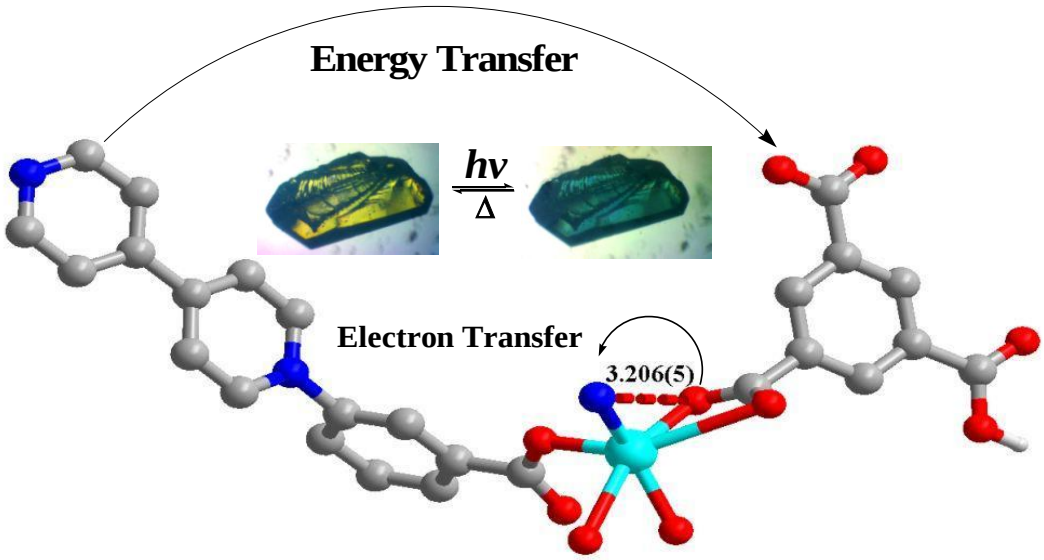

Fig. S3 The proposed photo-responsive mechanism**.**

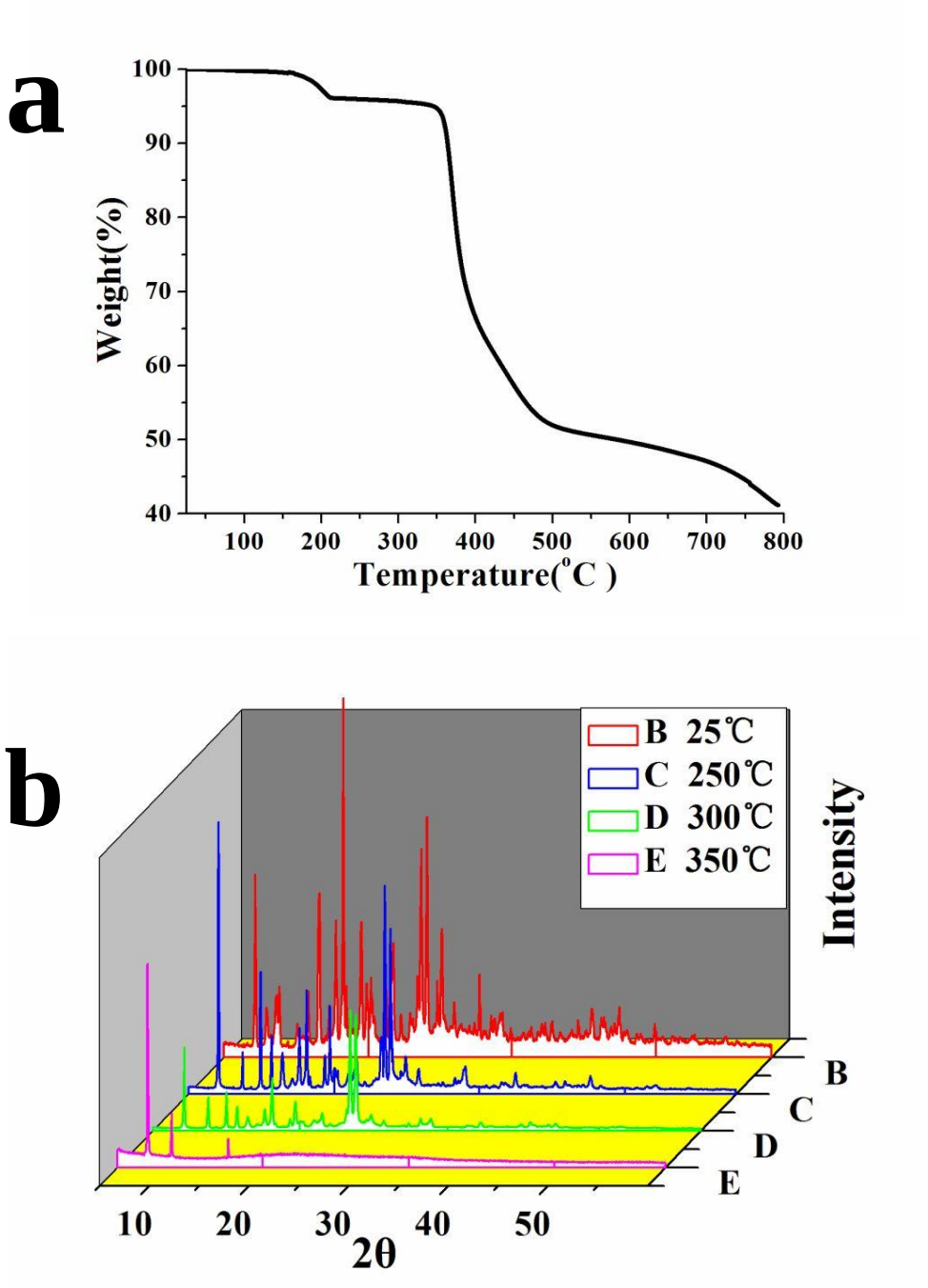

Fig. S4 (a) Thermal gravimetric curve of compound **1;** (b) Powder XRD patterns calcined at different temperatures.

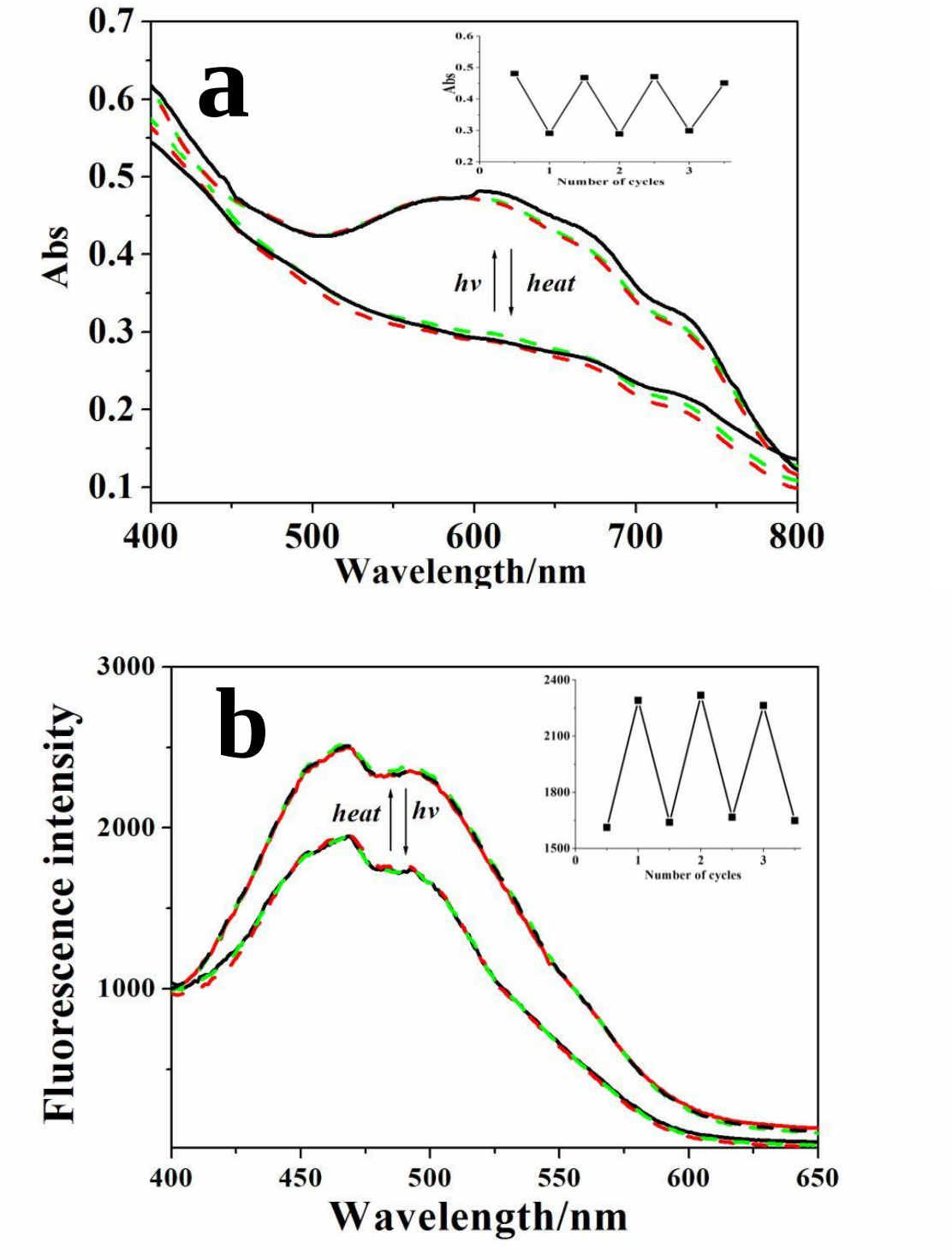

Fig. S5 (a) UV-Vis absorbance changes at 612 nm and (b) fluorescent emission changes at 500 nm for the sample of **1** on alternate excitation by photoirradiation at 365nm and heated at 170°C over three cycles in air.

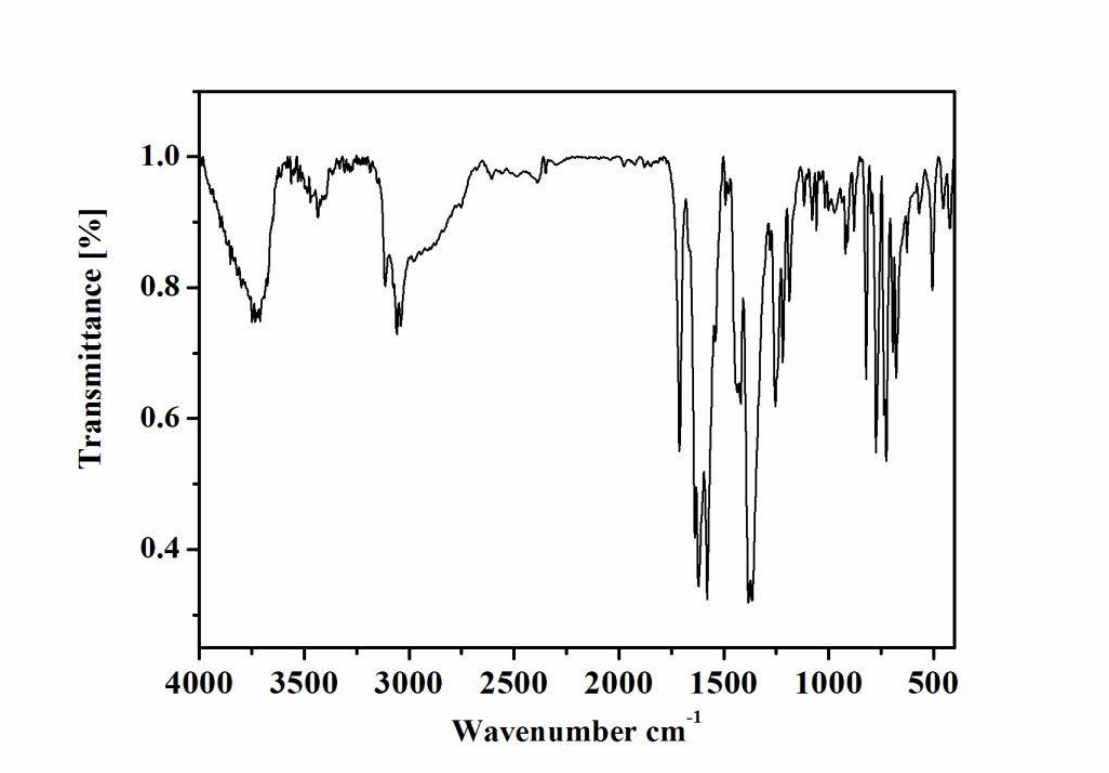

Fig. S6. IR spectrum of **1**

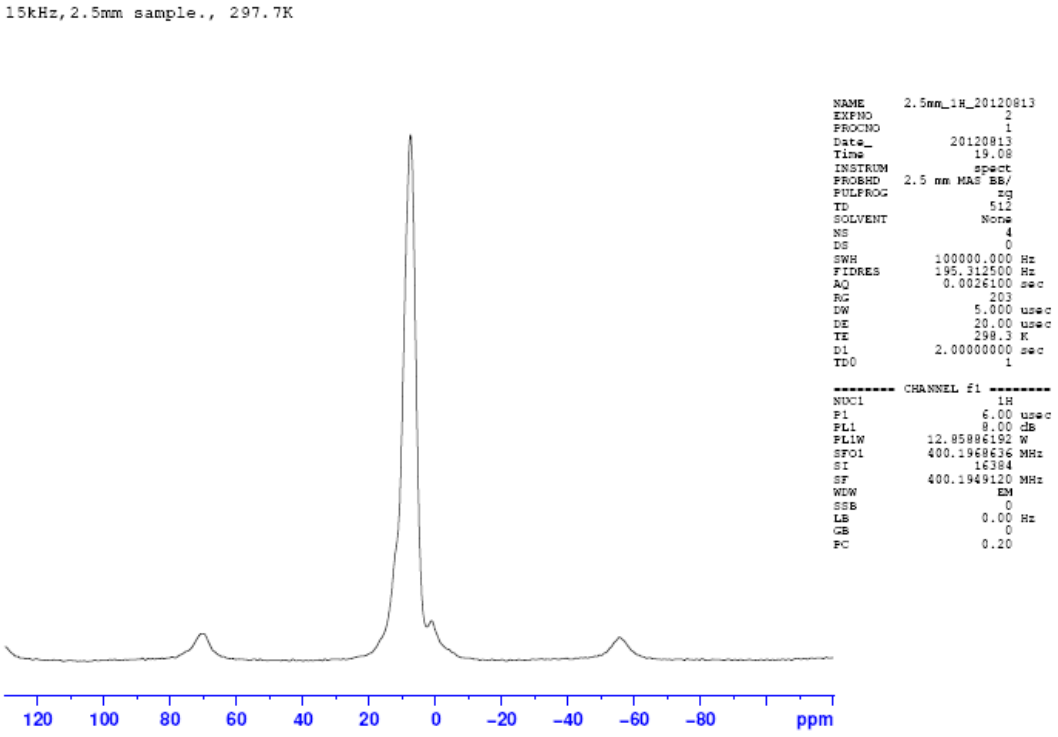

Fig. S7. Solid state ^{1}HNMR spectrum of **1**