Electronic Supporting Information

An Inorganic–Organic Hybrid Photochromic Material with Fast Response to Hard and Soft X-rays at Room Temperature†

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Content

Experimental

Materials and methods

All chemicals, except the $\mathbf{L^2}$ ligand, were of reagent grade quality and purchased from commercial sources without any further treatment. ^{1}H NMR analysis was determined on a Bruker-BioSpin AVANCE III NMR Spectrometer (400 MHz). Elemental analyses were performed on an Elementar Vario EL III microanalyzer. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was conducted using a METTLER TOLECO simultaneous TGA/DSC apparatus under N_2 with a ramp rate of 10 K·min^{-1}. UV–vis spectra were recorded in diffuse reflection mode on a PerkinElmer Lambda 950 UV/vis/NIR spectrophotometer equipped with an integrating sphere, and $BaSO_4$ plates were used as references (100% reflection). PXRD patterns were collected on a Rigaku MiniFlex 600 diffractometer powered at 40 kV and 15 mA using Cu-K_α X-ray (λ = 1.54056 Å). The simulated PXRD pattern was produced by the Mercury Version 3.9 software using the single-crystal X-ray diffraction data. ESR spectra were recorded on a Bruker-BioSpin E500 ESR spectrometer with a 100 kHz magnetic field in the X band (frequency of microwave, ~9.85 GHz) at room temperature. XPS studies were performed with a ThermoFisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al-K_α radiation (λ = 8.357 Å). The dosage of Mo-K_α X-ray generated from a Rigaku Pilatus 200K diffractometer was determined by an Inspector Alert™ nuclear radiation monitor with attenuators.

Single-crystal X-ray crystallography

Single-crystal X-ray diffraction measurement of **1** was performed on a Rigaku Pilatus 200K diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.710747 Å). Intensity data sets were collected using a ω scan technique, and corrected for *Lp* effects. The primitive structure was solved by the direct method using the Siemens SHELXTL-2014 suite.[1] The final structure was refined using a full-matrix least-squares refinement on F^2. Hydrogen atoms were generated geometrically. All non-hydrogen atoms were refined anisotropically. Crystallographic data and structural refinements for **1a** are summarized in Table S1†. Selected bond lengths for **1a** are listed in Table S2†.

The entry of CCDC-1587233 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: (Internet) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.

Synthesis of N,N'-dipropionate-4,4'-bipyridinium ($\mathbf{L^2}$).

Typically, a mixture of 4,4'-bipyridine (10 mmol, 1.562 g) and propenoic acid (100 mmol) was dissolved in 20 mL dichloromethane and stirred at room temperature for 2 d. After eliminating the dichloromethane solution, the yielded light yellow powder was sonicated in MeOH for 10 min, and then centrifuged before removing the clear solution. After repeating the sonicating and centrifuging processes for five times, the final powder was dried at 75 °C for 1 h. A NMR test proved that it was a pure phase of $\mathbf{L^2}$ (Fig. S11†). ^{1}H NMR (400 MHz, D_2O): δ = 9.12 (d, J = 6.8 Hz, 1H), 8.51 (d, J = 6.8 Hz, 1H), 4.91 (t, J = 6.60 Hz, 2H), 2.97 (t, J = 6.60 Hz, 2H). Note that the sample of $\mathbf{L^2}$ is easily hygroscopic.

Synthesis of $[Zn_2(L^2)Br_4]_n$ (1).

Typically, a mixture of $ZnBr_2$ (225 mg, 1 mmol) and $\mathbf{L^2}$ (150 mg, 0.5 mmol) was dissolved in H_2O and DMF (v:v = 3:2) with stirring for 30 min, and then the filtrate was transferred into a glass beaker that was covered with a porous preservative film. After slow evaporation at room temperature for several days, light yellow prismatic crystals of **1** were obtained. Yield (based on $\mathbf{L^2}$): >50 %. PXRD (Fig. S5†) and elemental analysis data indicated that the as-synthesized crystalline sample was a pure phase. Anal. Calcd (%) for **1**: C, 25.60; H, 2.15; N, 3.73. Found (%):

C, 25.12; H, 2.25; N, 3.35. Unlike **L^2**, compound **1** is air stable. A TGA illustrated that compound **1** had no weight loss below ~265 °C (Fig. S12†).

Table S1 Crystal and structure refinement data for **1** before coloration.

Chemical formula	$C_{16}H_{16}Br_4N_2O_4Zn_2$
M_r	750.69
Crystal size (mm)	0.35 × 0.28 × 0.26
Crystal system	Triclinic
Space group	$P\bar{1}$
Temperature (K)	293
a (Å)	6.849(2)
b (Å)	12.673(4)
c (Å)	13.419(4)
α (deg)	78.619(13)
β (deg)	86.759(15)
γ (deg)	86.386(17)
V (Å^3)	1138.4(6)
Z	2
F(000)	716
Radiation type	Mo-K_α
μ (mm^{-1})	9.15
Diffractometer	Rigaku Pilatus 200K
Absorption correction	Multi-scan Sphere (Rigaku *CrystalClear*)
Abs coeff (mm^{-1})	9.150
R_{int}	0.067
R_1[a]	0.069
ωR_2[b]	0.207
GOF on F^2	1.00
No. of reflections	4972
No. of parameters	253

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $\omega R_2 = \{\sum\omega[(F_o)^2-(F_c)^2]^2/\sum\omega[(F_o)^2]^2\}^{1/2}$.

Table S2 Selected bond lengths [Å] for **1** before coloration.

Bond	Length /Å
Zn1—O21	2.021(5)
Zn1—O12	2.047(5)
Zn1—Br11	2.3444(14)
Zn1—Br12	2.3547(13)
Zn2—Br22	2.4029(15)
Zn2—Br21	2.3592(13)
Zn2—O22	1.967(6)
Zn2—O12	2.016(5)
C18—O11	1.204(8)
C18—O12	1.320(9)
C28—O22	1.233(9)
C28—O21	1.243(9)

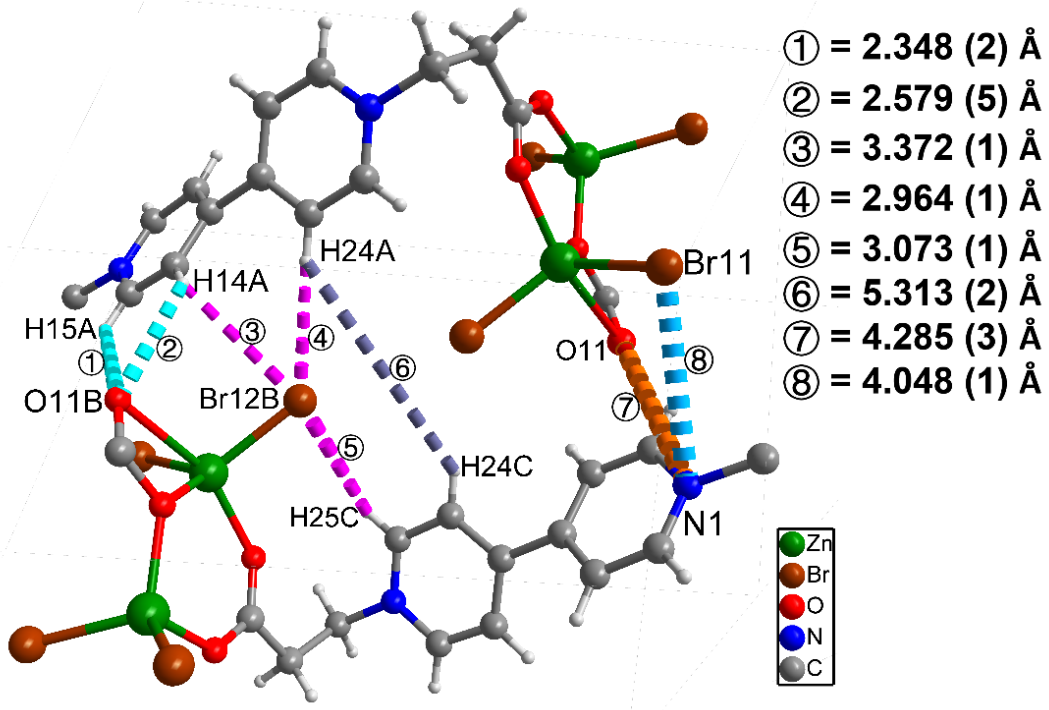

Fig. S1 The H-bonds (①②③④⑤) and shortest distances of H···H (⑥), O···N (⑦) and Br···N (⑧) between two adjacent chains. Symmetry codes: (A) X, Y, 1+Z; (B) 1–X, 1–Y, 1–Z; (C) 1–X, 1–Y, –Z.

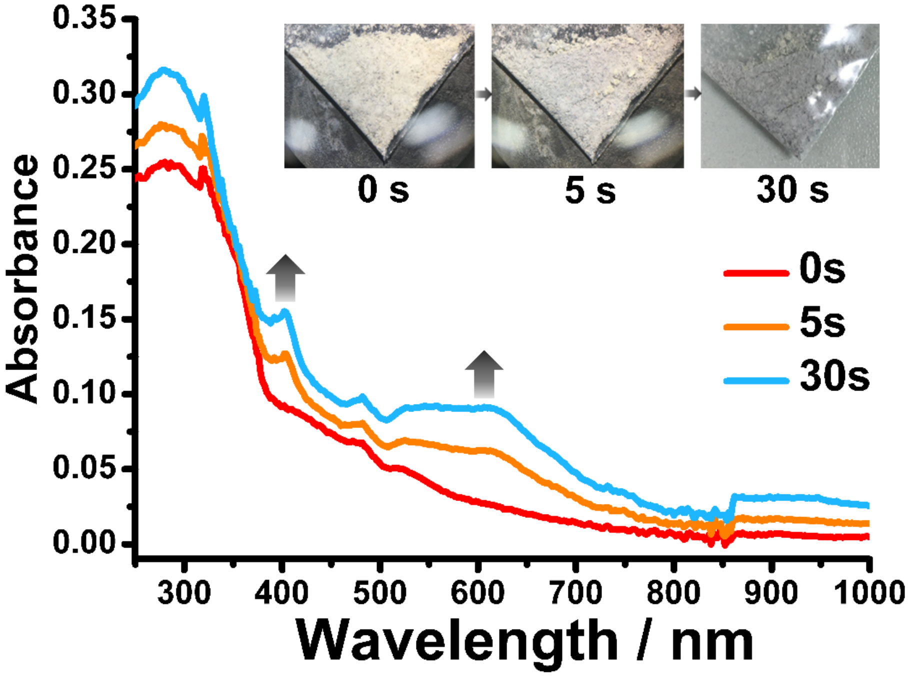

Fig. S2 Time-dependent UV–vis spectra of **L^2** upon irradiation of the 300 W Xenon lamp. Inset: Photographs of **L^2** captured at different exposing time.

Fig. S3 A photoresponsive range test for **1a** in the UV–vis region conducted on a single-grating Edinburgh EI920 fluorescence spectrometer equipped with a 450 W Xe lamp. Each spot was irradiated for 20 min.

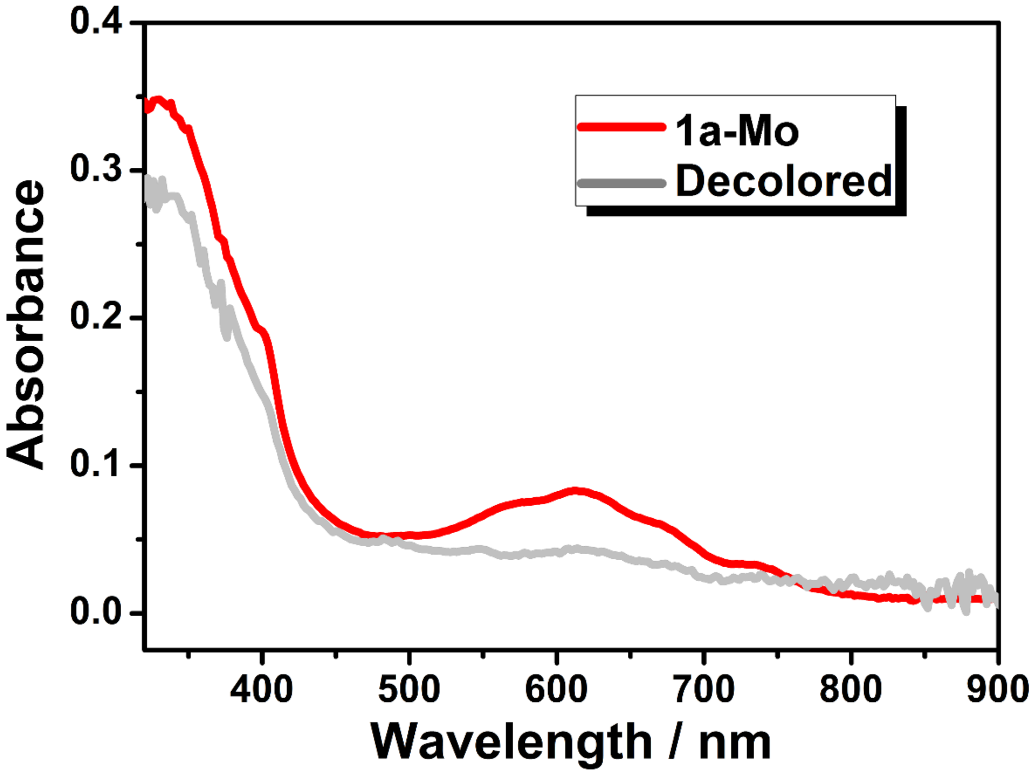

Fig. S4 UV-vis absorption spectra of **1a-Mo** and the **decolored** sample.

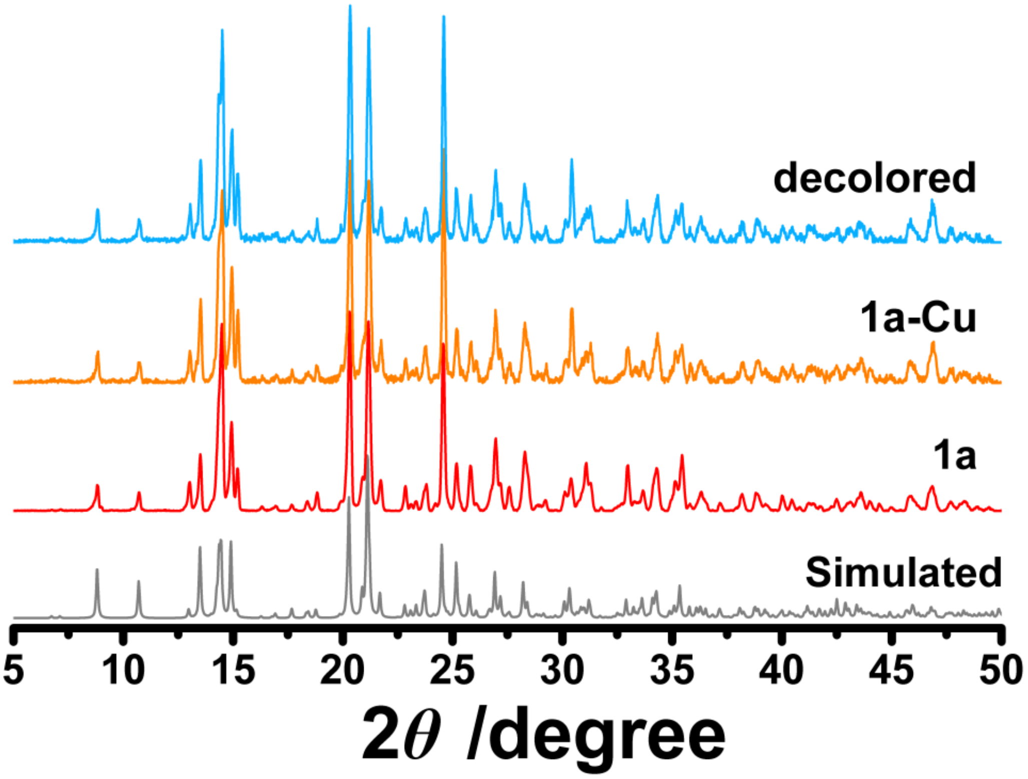

Fig. S5 PXRD patterns of **1a**, **1a-Cu**, and the **decolored** sample**.** For comparison, the simulated result from the single-crystal diffraction data is also shown.

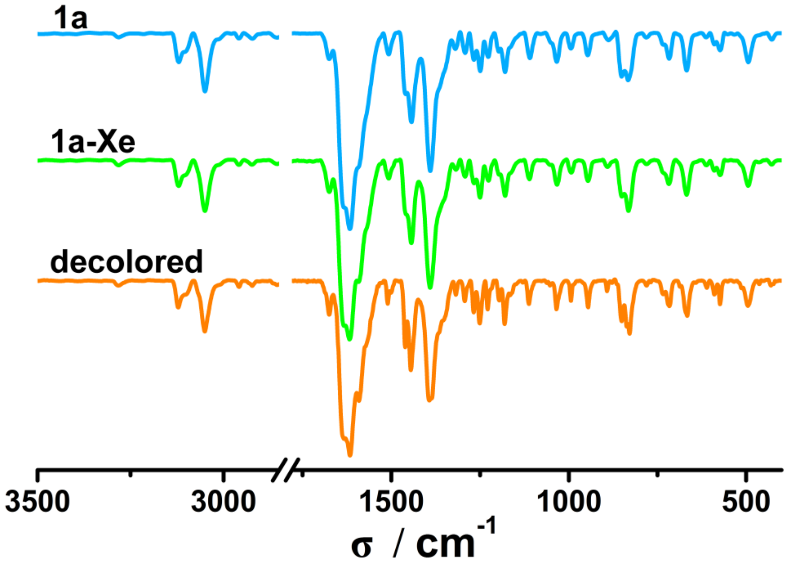

Fig. S6 IR spectra of **1a**, **1a-Xe**, and the **decolored** sample**.**

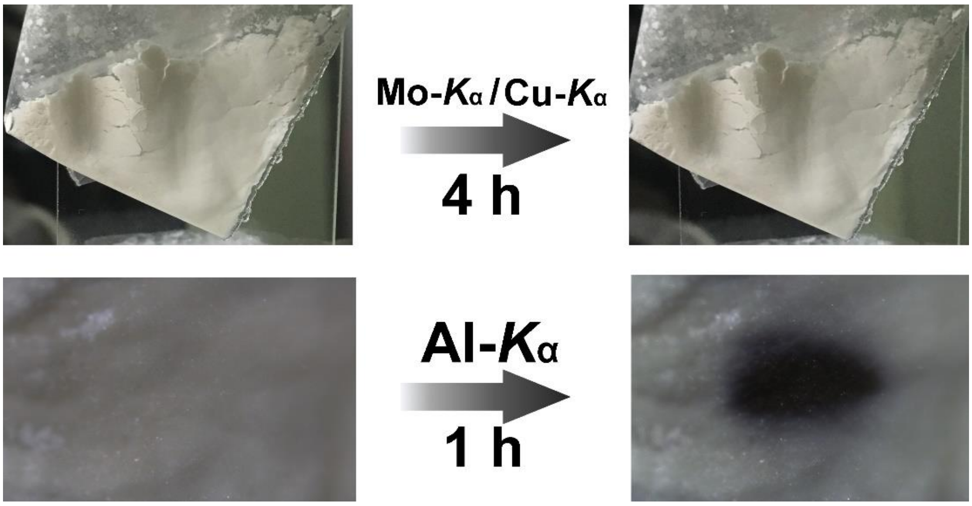

Fig. S7 Photos of the samples of the **L^2** ligand before and after irradiation of Mo/Cu-K_α (4 h) and Al-K_α (1 h) X-rays.

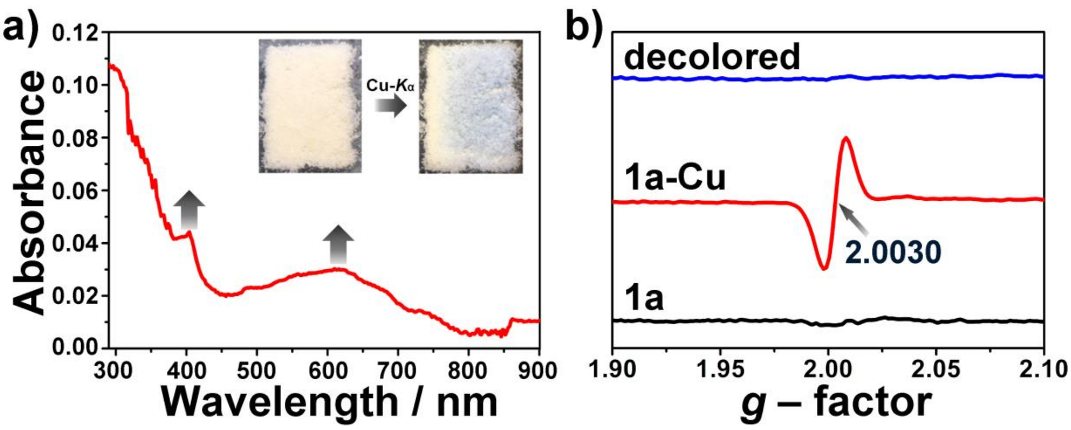

Fig. S8 a) UV-vis spectrum of **1a-Cu**. Inset: Photographs showing the X-ray-induced coloration. b)

ESR curves of **1a, 1a-Cu** and the **decolored** sample.

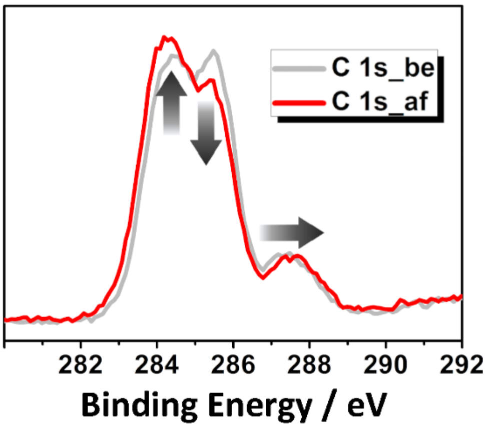

Fig. S9 *In situ* measurement of C 1s XPS core-level spectra of **1** before (**1a**) and after irradiation (**1a-Al**) of Al-K_α X-ray for 30 min (λ =8.357 Å; powered at 150 W. The arrows denote the shift. Due to the fast coloration process upon irradiation of Al-K_α X-ray, no fitting was taken out.

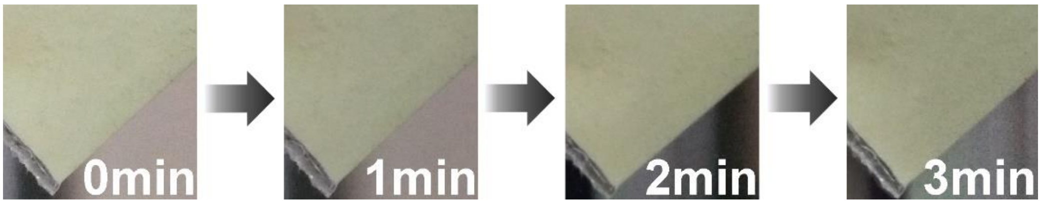

Fig. S10 Time-dependent coloration of **1** under Mo-K_α irradiation, which showed that **1a** did not experienced clear color change in 3 min.

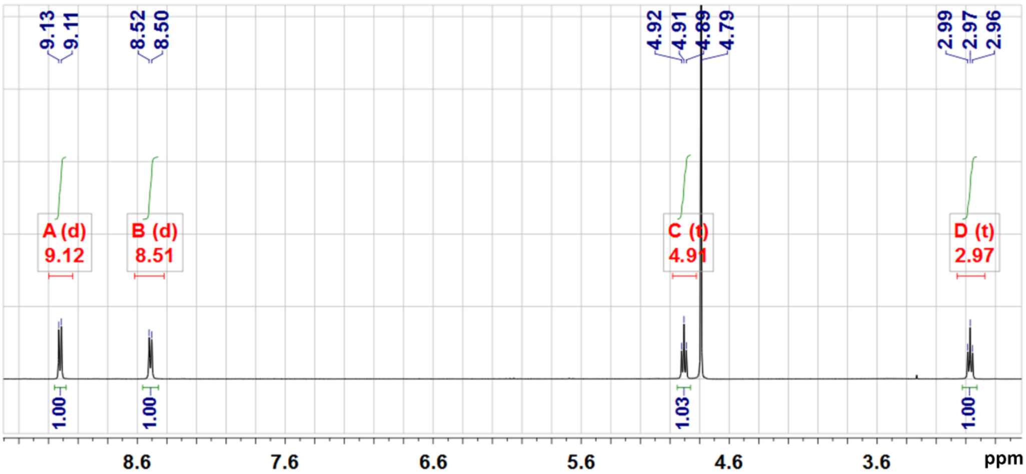

Fig. S11 ^{1}H NMR spectrum of **L**^{2}.

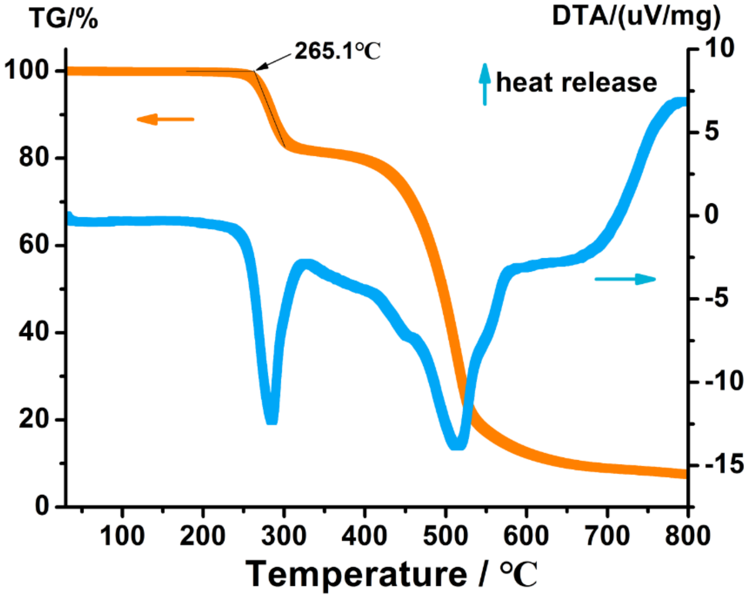

Fig. S12 Thermogravimetric analysis (TGA) of **1** in the N_2 atmosphere.

References

1 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.