Electronic Supplementary Material (ESI) for CrystEngComm
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Support Information

Diplex Single Crystal to Single Crystal Transformation by Different Inducement

Guan-E Wang,[a,b] Gang Xu,[a] Pei-Xin Li,[a] Shuai-Hua Wang,[a] Ming-Sheng Wang,[a] Guo-Cong Guo,*[,a] Jin-Shun Huang[a]

a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

b Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

E-mail: gcguo@fjirsm.ac.cn

Experimental section:

1. Materials

PbI_2, $CuCl_2 \cdot 2H_2O$, 2,2'-Bipyridine, HI, ethanol, *N*, *N*'-dimethyl formamide (DMF) methanol were received from Sinopharm Chemical Reagent Co. Ltd.. They were directly used without further purification. Water was deionized and distilled before use.

2. Synthesis of crystalline $[Cu(2,2'\text{-Bipy})_2I]_n(PbI_3)_n \cdot n DMF \cdot n H_2O$ (2,2'-Bipy = 2,2'-Bipyridine; DMF = N,N-dimethyl formamide) (1)

A mixture of PbI_2 (0.116 g, 0.125 mmol), $CuCl_2 \cdot 2H_2O$ (0.045 g, 0.125mmol), 2,2'-Bipy (0.079 g, 0.25 mmol), DMF (3 mL), and concentrated HI (1.5 mL, 45%) was heated at 150 °C for 2 days in a sealed 25-mL Teflon-lined stainless steel vessel. Upon cooling at 2.5 °C·h^{-1} to room temperature, dark green sheet crystals of **1** were obtained in 95% yield (based on PbI_2). Elem. Anal. (%) Calcd.: C:23.35, H: 2.12, N: 5.92;. Found: C: 23.24; H: 2.07; N: 5.86. IR (KBr, cm^{-1}): 3901 (w), 3869 (w), 3848 (w), 3818 (w), 3758 (w), 3738 (w), 3677 (w), 3647 (w), 3442 (s), 3064 (w), 2922 (m), 2856 (w), 1662 (s), 1592 (s), 1466 (m), 1437 (s), 1387 (m), 1308 (m), 1242 (w), 1149 (w), 1097 (w), 1018 (w), 767 (m), 721 (m), 662 (w). Its phase purity was verified by elemental analysis, IR spectrum, thermogravimetric analysis (TG), and

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powder X-ray diffraction (PXRD) determination (Fig. S1). The TG curves (Fig. S13) show that the first weight loss (7.17%) between 98 ^{o}C and 130 ^{o}C corresponds to the loss of DMF and water molecules (calcd 7.7%).

The synthesis time period of **1** has been elongated (heated at 150 °C for 6 days, with a cooling speed at 2.5 °C·h^{-1} to room temperature) and repeated for three times to try to synthesize **1**a or **1**b directly. All of the results of these experiments show that only compound **1** can be obtained, so it was not an *in situ* transformation of **1** to **1b** under hydrothermal conditions or to the conversion of **1a** to **1b**. The result was proved by randomly selected single crystals cell parameters (Table S1) and PXRD (Figure S14).

3. Synthesis of crystalline $[Cu(2,2'\text{-Bipy})_2I]_n(PbI_3)_n$ (1a)

Compound **1a** was synthesized by heating compound **1** at 150 °C for 5 hours. The structure was confirmed by PXRD (Fig. S1). Elem. Anal. (%) Calcd.: C:22.06, H: 1.47, N: 5.13;. Found: C: 22.25; H: 1.54; N: 5.20. IR (KBr, cm^{-1}): 3901 (w), 3871 (w), 3851 (w), 3821 (w), 3750 (w), 3669 (w), 3649 (w), 3619 (w), 3589 (w), 3559 (w), 3439 (w), 2918 (w), 1592 (m), 1493 (w), 1466 (m), 1434 (s), 1308 (m), 1242 (w), 1149 (w), 1018 (w), 754 (s), 714 (m), 642 (w).

4. Synthesis of crystalline $[Cu(2,2'\text{-Bipy})_3]_n(Pb_2I_6)_n$ (1b)

Compound **1b** was synthesized by dipping compound **1** in methanol or water solution for 2 months. IR (KBr, cm^{-1}): 3851 (w), 3743 (w), 3669 (w), 3644 (w), 3557 (w), 3438 (w), 2918 (w), 2848 (w), 2489 (w), 1772 (w), 1442 (s), 1155 (w), 1079 (w), 1051 (w), 1001 (w), 881 (m), 771 (w), 759 (w), 734 (w), 696 (w), 645 (w), 621 (w).

Compound **1b** can also be synthesized by dipping compound **1** in other solution such as phenylcarbinol, propanol, tetrahydrofuran, butanol, etc, or by these mixed solutions. The SCSC transformation can occur at room temperature. The SCSC transformation time will be shortened under a little higher temperature (40 ^{o}C, 1.5 month). Compound **1b** is stable in methanol, water, and phenylcarbinol *etc* solutions.

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5. Measurements.

PXRD pattern was collected on a MiniFlex II diffractometer using Cu-K_α radiation (λ = 1.5406 Å) at 30 kV and 15 mA. The simulated pattern of **1** was derived from the Mercury Version 1.4 software (http://www.ccdc.cam.ac.uk/products/mercury/). The analyses of carbon, nitrogen and hydrogen contents were performed on an Elementar Vario MICRO microanalyser. Thermogravimetry analyses were made on a Netzsch STA449C simultaneous TG-DTA apparatus under an N_2 atmosphere with each sample heated in an Al_2O_3 crucible at a heating rate of 10 K·min^{-1}. The FT-IR spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer using KBr disks in the range of 4000−400 cm^{-1}. The DSC analyses were made on NETZSCH DSC 204F1 Phoenix under an N_2 atmosphere with each sample heated in an Al crucible at a heating rate of 10 K·min^{-1}. The ions concentrations of Cu and Pb in the methanol solution after dipping the crystals **1** for 1 month had been tested on Ultima 2 Inductively Coupled Plasma OES spectrometer. The ions concentrations of Cu and Pb in the pure methanol solution were also tested (Fig. S12).

6. X-ray crystallographic study

The X-ray diffraction measurements of **1, 1a,** and **1b** were performed on a Rigaku Ultrax-Saturn 70 diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data sets were collected using an ω scan technique and corrected for *Lp* effects. The primitive structures were solved by the direct method using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software. The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The final structures were refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon and nitrogen atoms were generated geometrically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 891591−891593. This datum can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting graphics:

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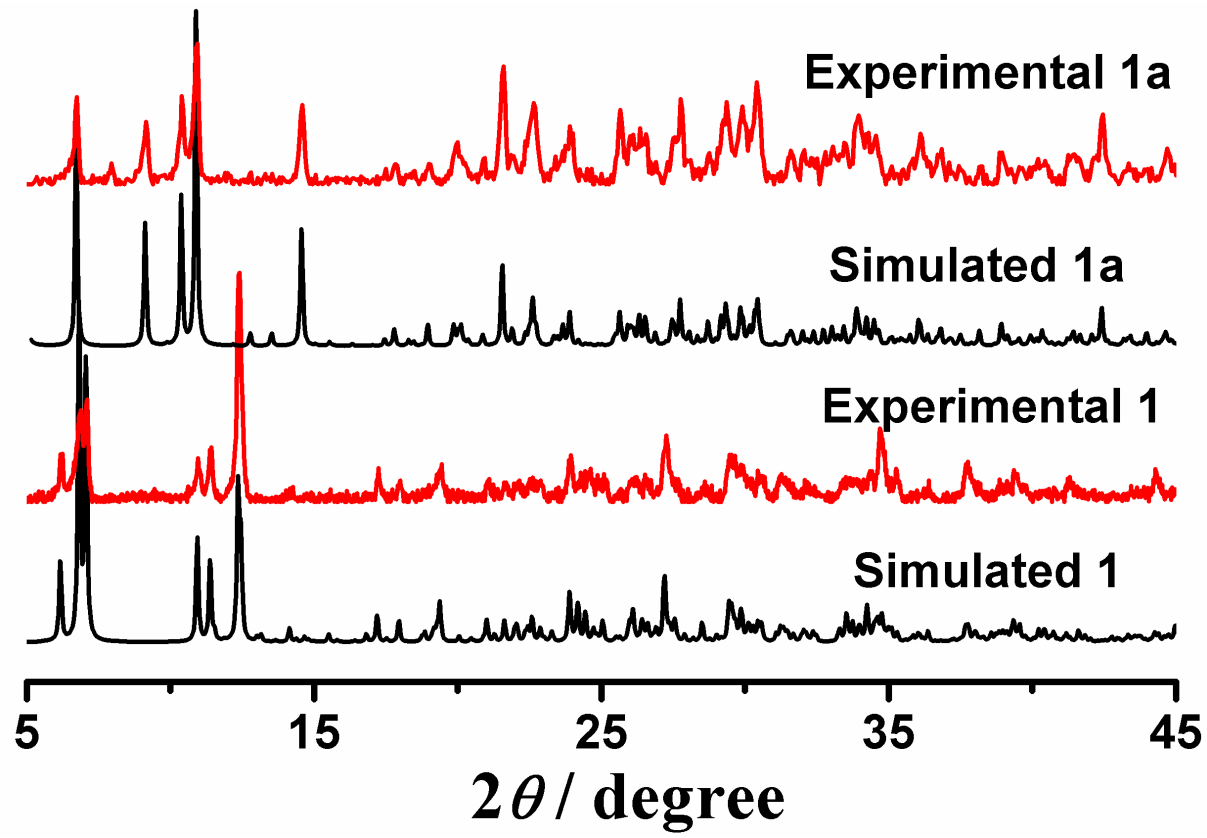

Fig. S1 PXRD patterns for **1** and **1a**.

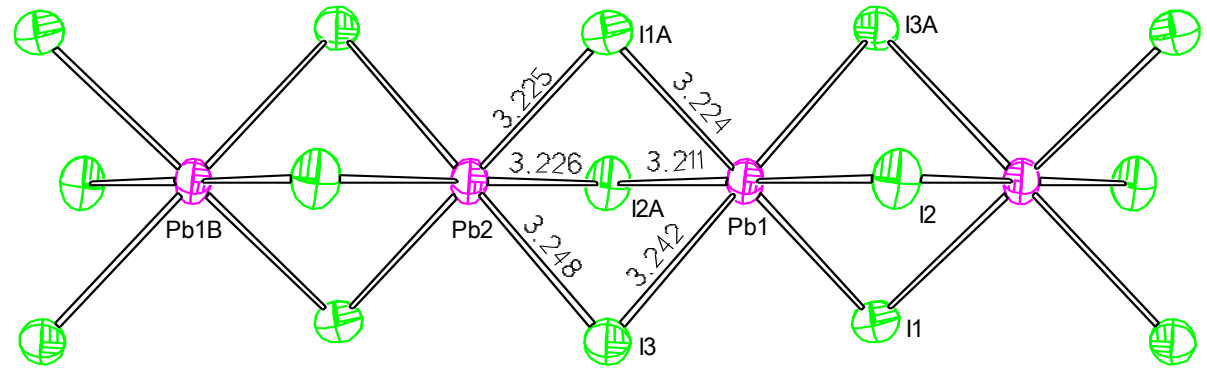

Fig. S2 1-D chain structure of iodoplumbate ion in **1** extending along the *c* axis. Symmetry codes: A: 1-x, 1-y, -z; B: x, y, -1+z.

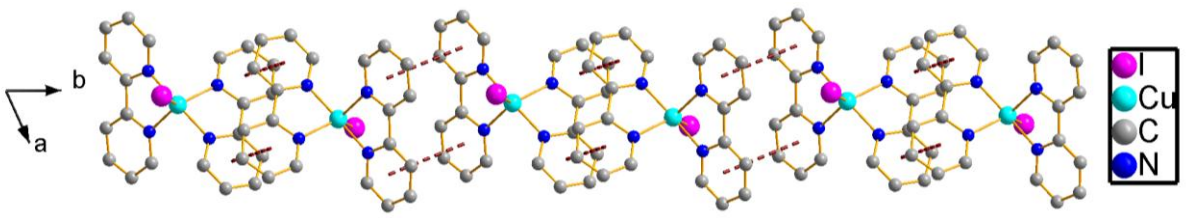

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Fig. S3 The face-to-face π···π interactions of $Cu(2,2'\text{-Bipy})_2I^+$ cations in 1-D $[Cu(2,2'\text{-Bipy})_2I]^+$ supramolecular chain with hydrogen atoms being omitted for clarity.

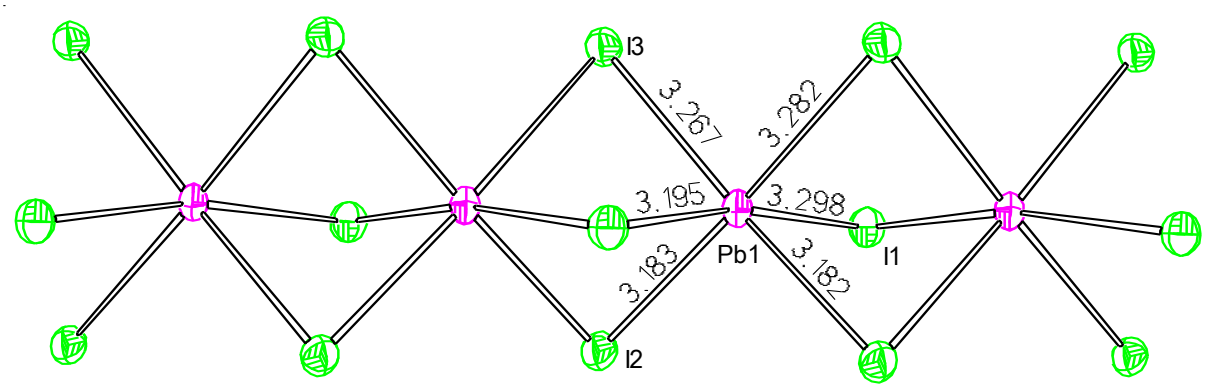

Fig. S4 1-D chain structure of iodoplumbate ion in **1a** extending along the *c* axis.

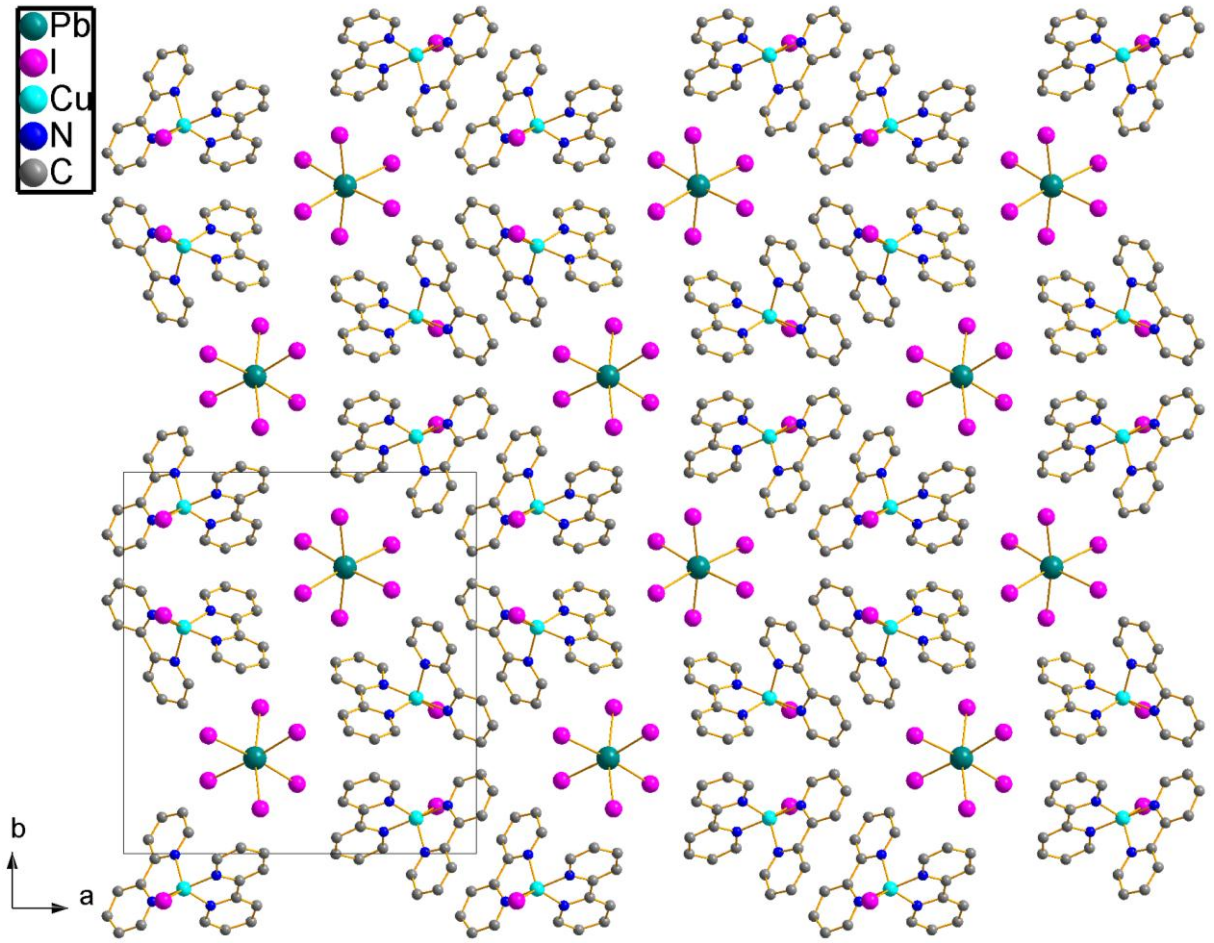

Fig. S5 Crystal structure of **1a** viewed along the *c* axis. Hydrogen atoms are omitted for clarity.

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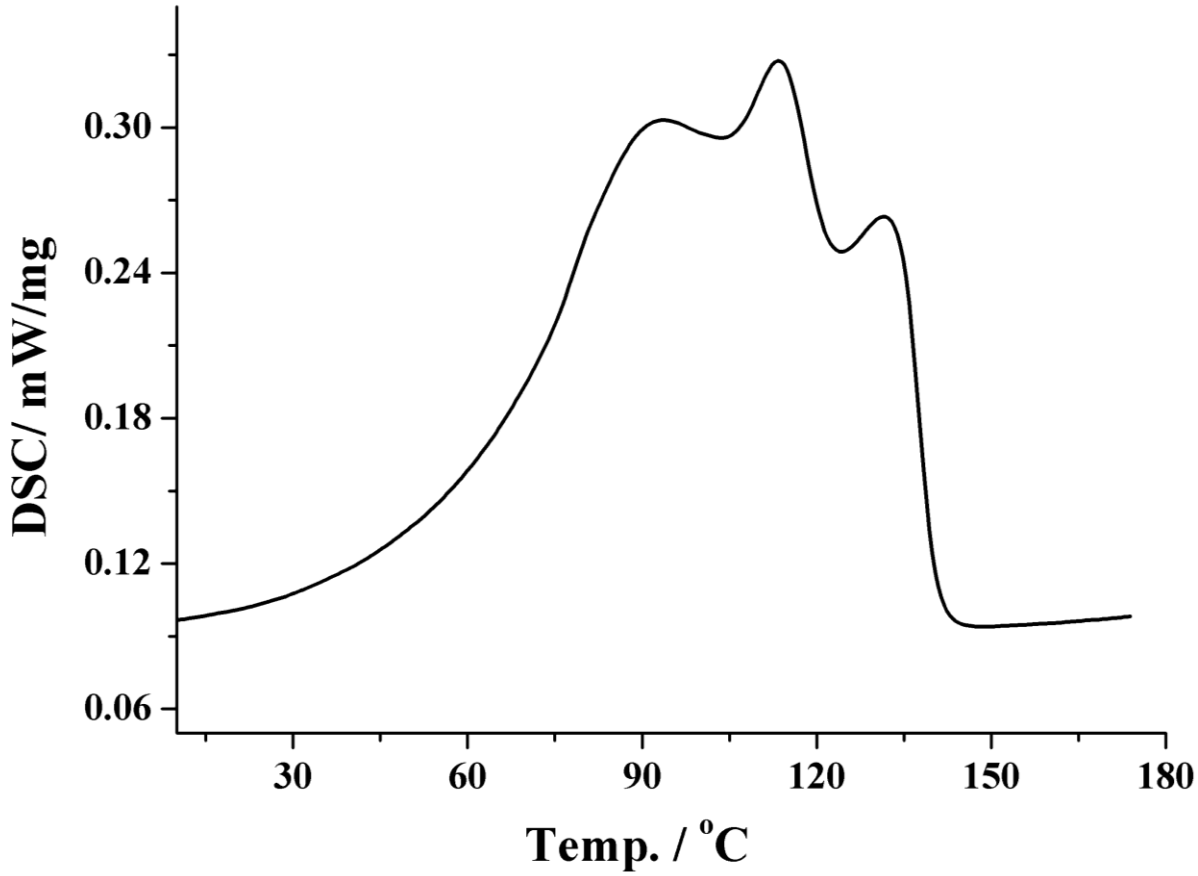

Fig. S6 DSC curve of a crystal **1**.

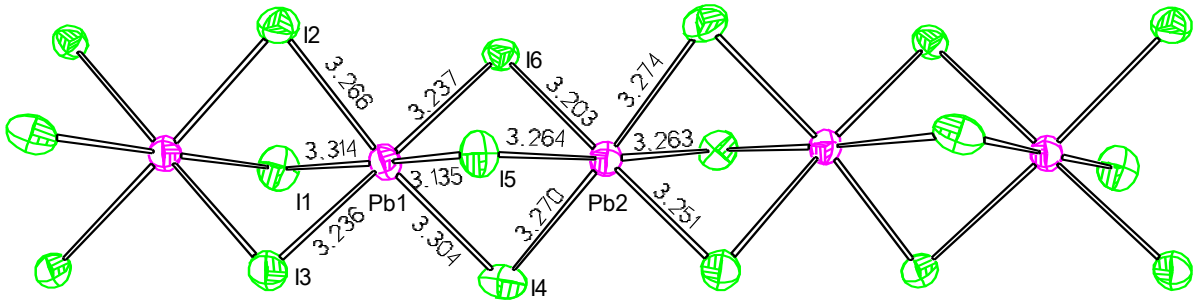

Fig. S7 1-D chain structure of iodoplumbate ion in **1b** extending along the *c* axis. Symmetry codes: A: x, 3/2−y, −1/2+z.

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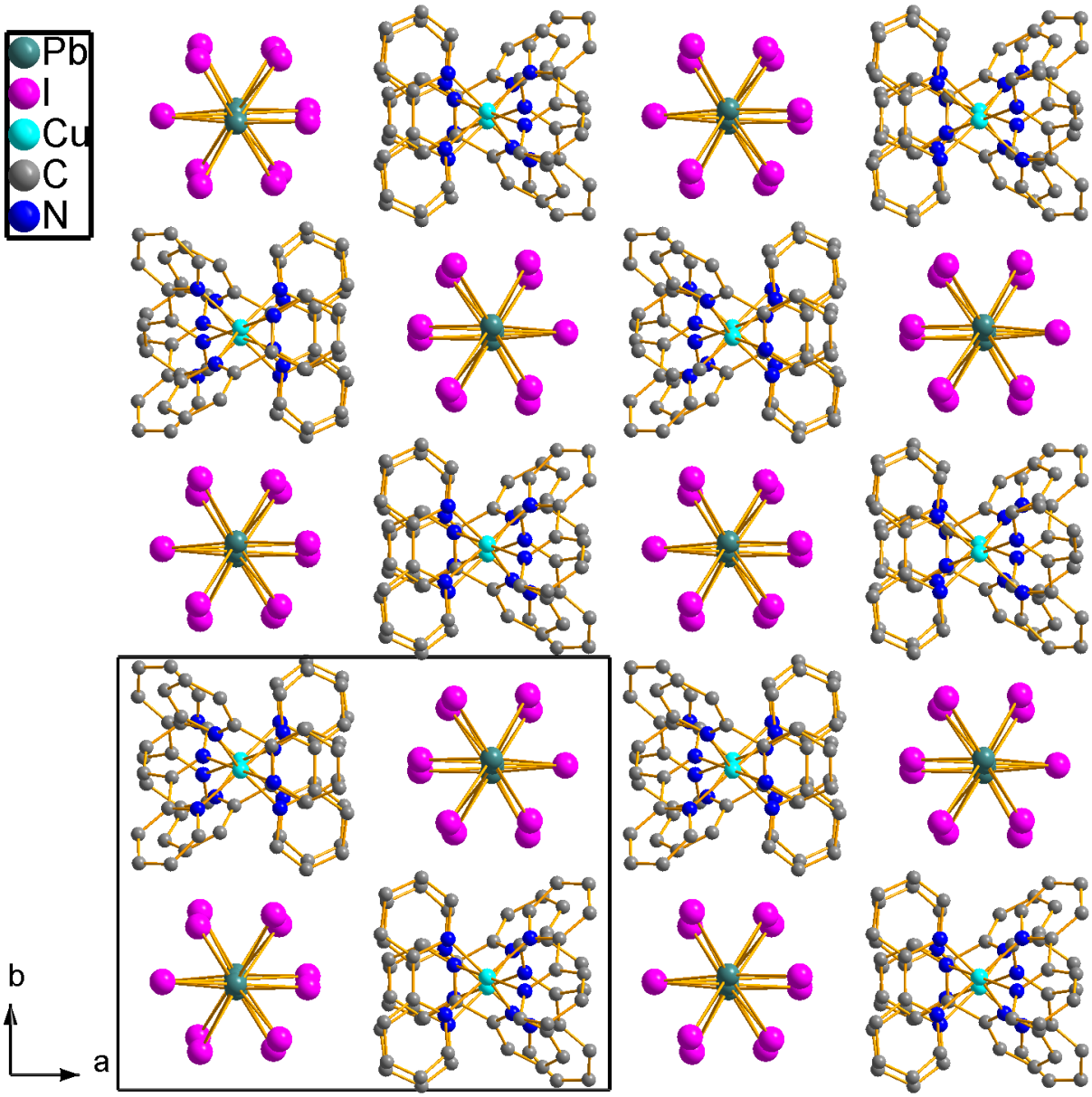

Fig. S8 Crystal structure of **1b** viewed the *c* axis.

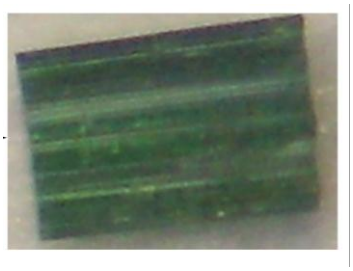

Fig. S9 The photograph of a crystal of **1** dipped in methanol solution for 1 month.

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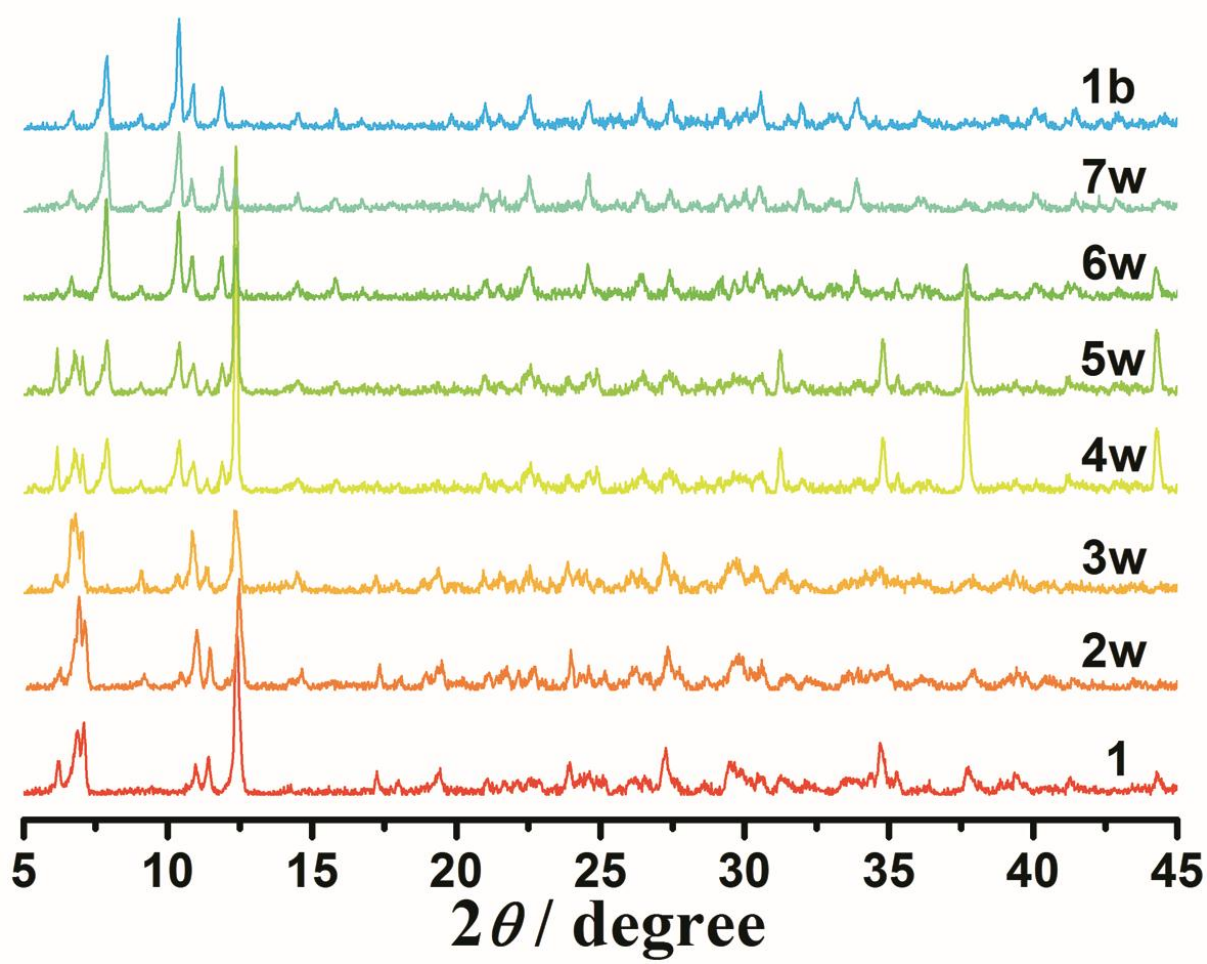

Fig. S10 The PXRD spectra of **1** with different dipping time (from 2 weeks to 7 weeks).

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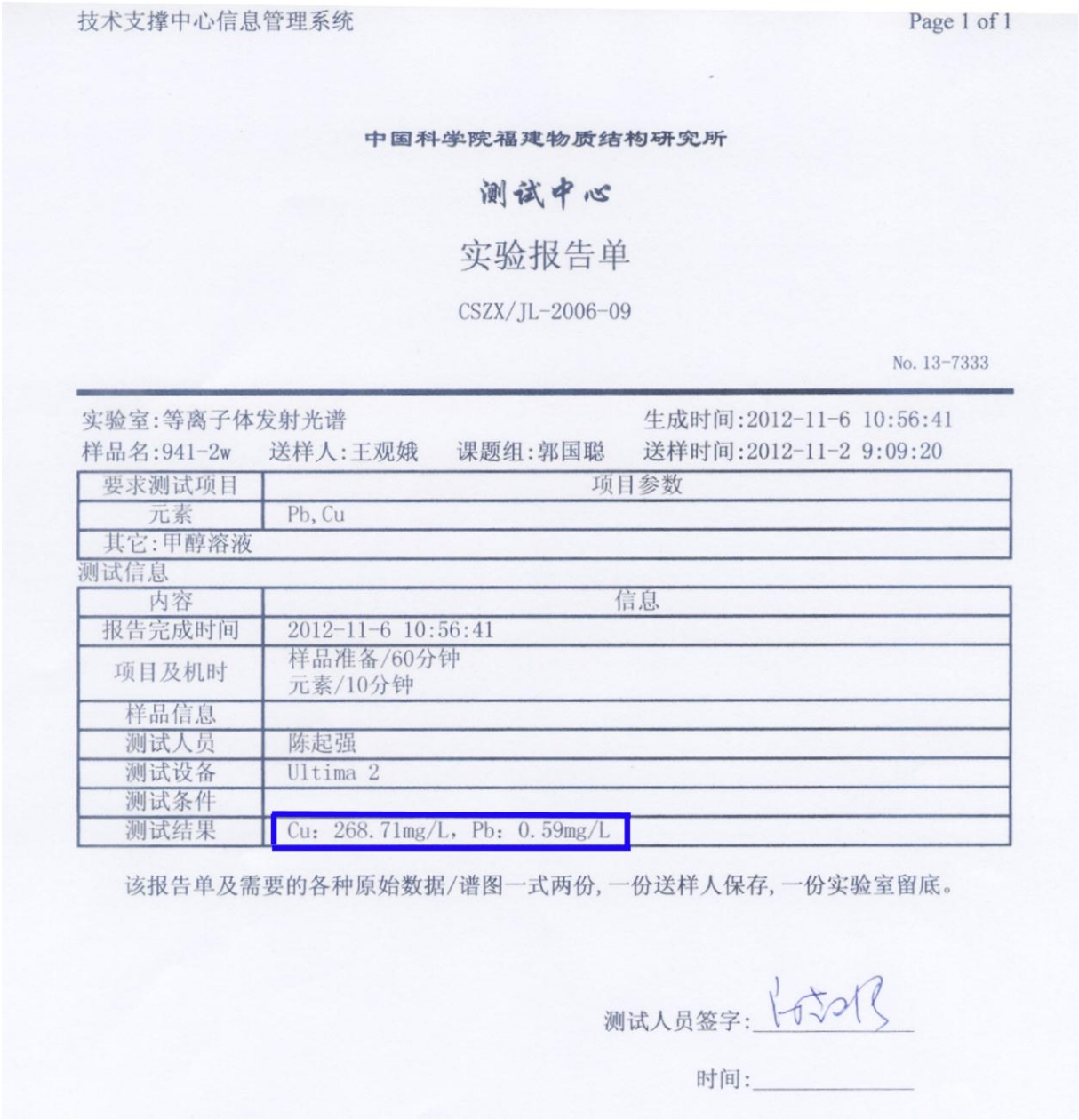

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中国科学院福建物质结构研究所

测试中心

实验报告单

CSZX/JL-2006-09

No. 13-7333

实验室:等离子体发射光谱 生成时间:2012-11-6 10:56:41

样品名:941-2w 送样人:王观娥 课题组:郭国聪 送样时间:2012-11-2 9:09:20

要求测试项目	项目参数
元素	Pb, Cu
其它:甲醇溶液	

测试信息

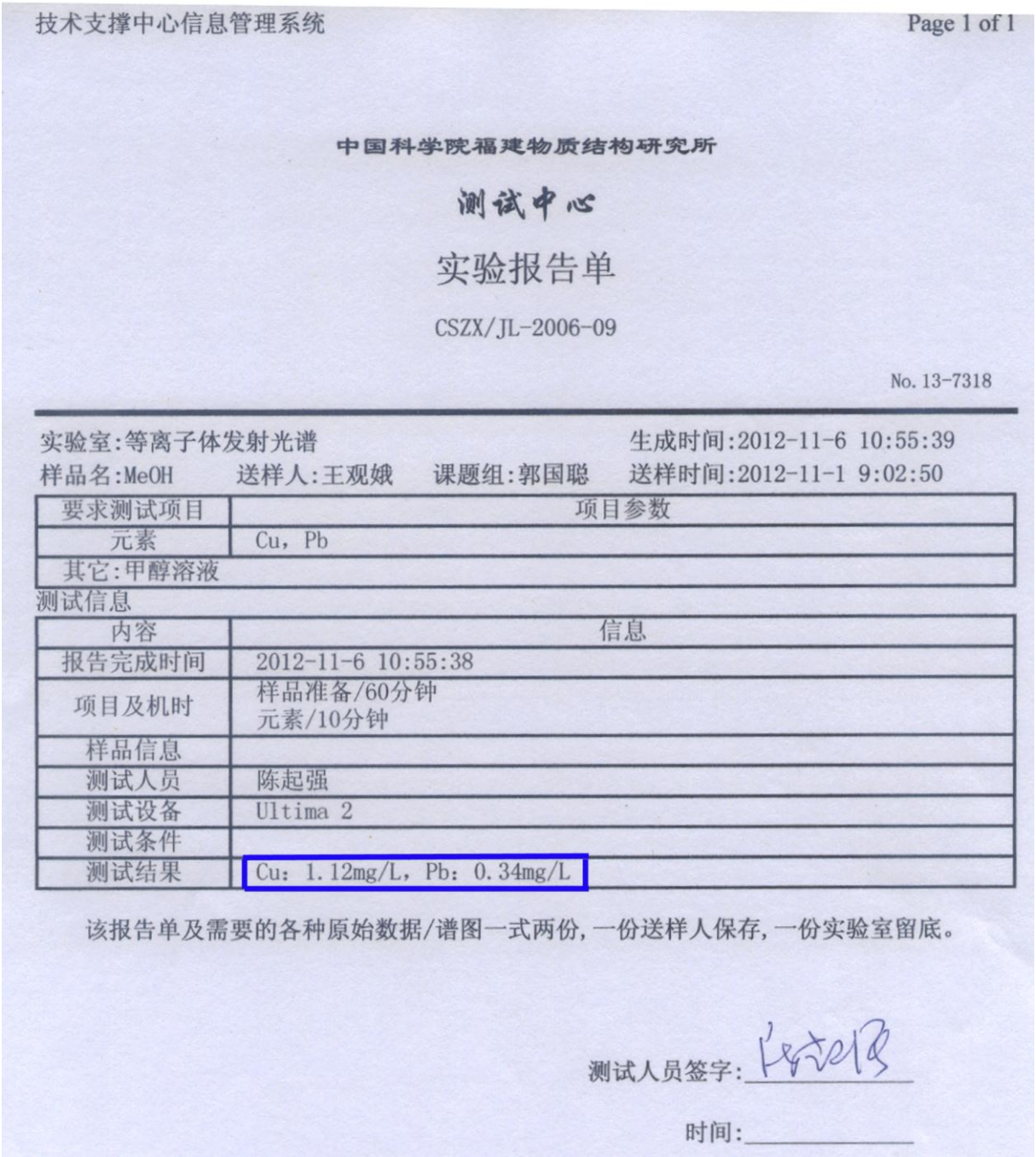
内容	信息
报告完成时间	2012-11-6 10:56:41
项目及机时	样品准备/60分钟 元素/10分钟
样品信息	
测试人员	陈起强
测试设备	Ultima 2
测试条件	
测试结果	Cu: 268.71mg/L, Pb: 0.59mg/L

该报告单及需要的各种原始数据/谱图一式两份,一份送样人保存,一份实验室留底。

测试人员签字:

时间:

Fig. S11 The ions concentrations of Cu and Pb in the methanol solution (300 mg of crystals **1** dipping in 20 mL methanol solution for 1 month).



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中国科学院福建物质结构研究所

测试中心

实验报告单

CSZX/JL-2006-09

No. 13-7318

实验室:等离子体发射光谱 生成时间:2012-11-6 10:55:39

样品名:MeOH 送样人:王观娥 课题组:郭国聪 送样时间:2012-11-1 9:02:50

要求测试项目	项目参数
元素	Cu, Pb
其它:甲醇溶液	

测试信息

内容	信息
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项目及机时	样品准备/60分钟 元素/10分钟
样品信息	
测试人员	陈起强
测试设备	Ultima 2
测试条件	
测试结果	Cu: 1.12mg/L, Pb: 0.34mg/L

该报告单及需要的各种原始数据/谱图一式两份,一份送样人保存,一份实验室留底。

测试人员签字:

时间:

Fig. S12 The ions concentrations of Cu and Pb in the pure methanol solution.

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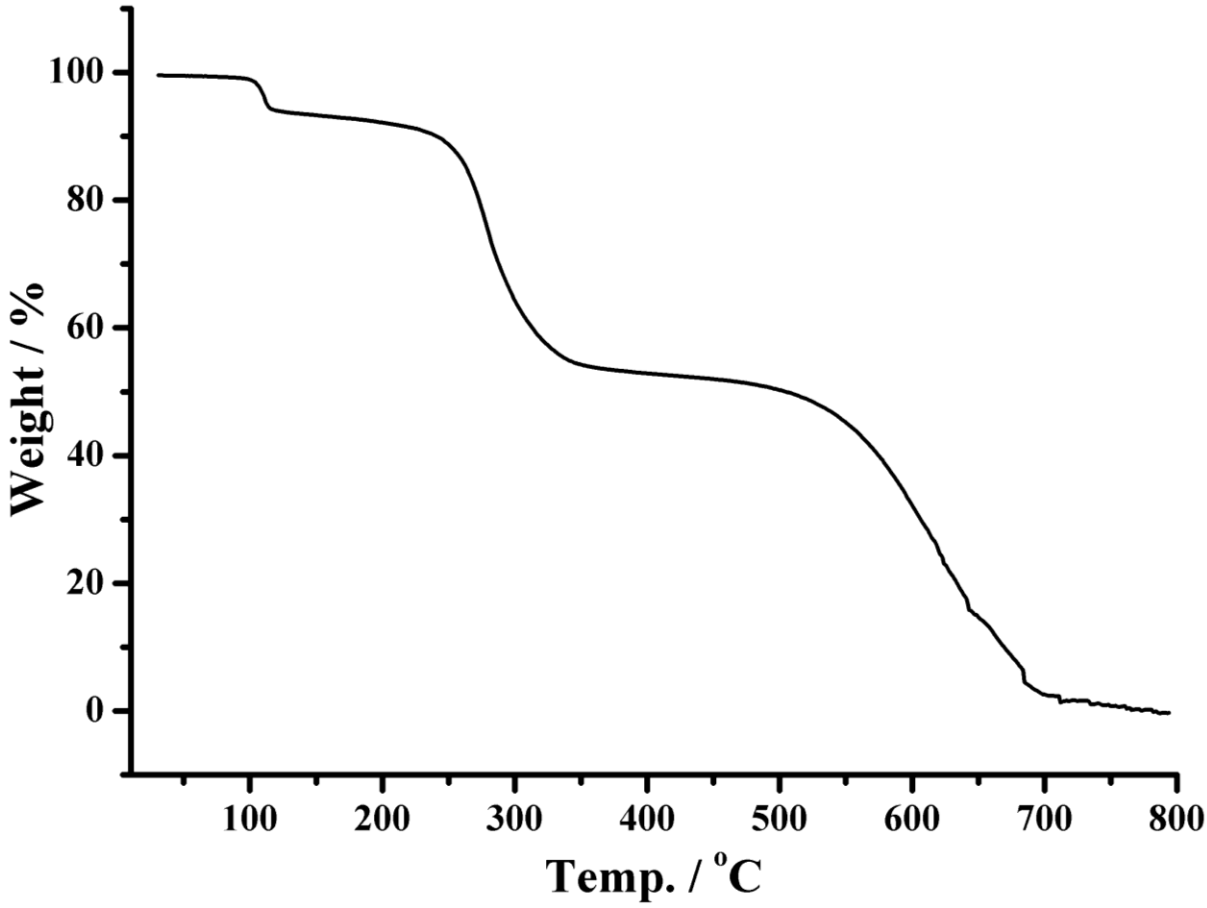

Fig. S13 TG curve of **1**.

Table S1. The randomly selected single crystals cell parameters of prolonged synthesized **1**.

times	*a*(Å)	*b*(Å)	*c*(Å)	*α*	*β*	*γ*	V(Å^3)
Compound **1**	7.995(3)	14.713(5)	15.860(5)	111.18(3)	97.66(1)	104.95(3)	1626.8(9)
Elongated synthesis 1	7.985(3)	14.681(5)	15.855(5)	111.22(1)	97.71(1)	105.12(1)	1617.7(9)
Elongated synthesis 2	7.995(1)	14.681(1)	15.870(1)	111.07(1)	97.90(1)	105.17(1)	1621.31(3)
Elongated synthesis 3	7.986(1)	14.657(1)	15.860(1)	111.14(1)	97.85(1)	105.14(1)	1615.69(2)

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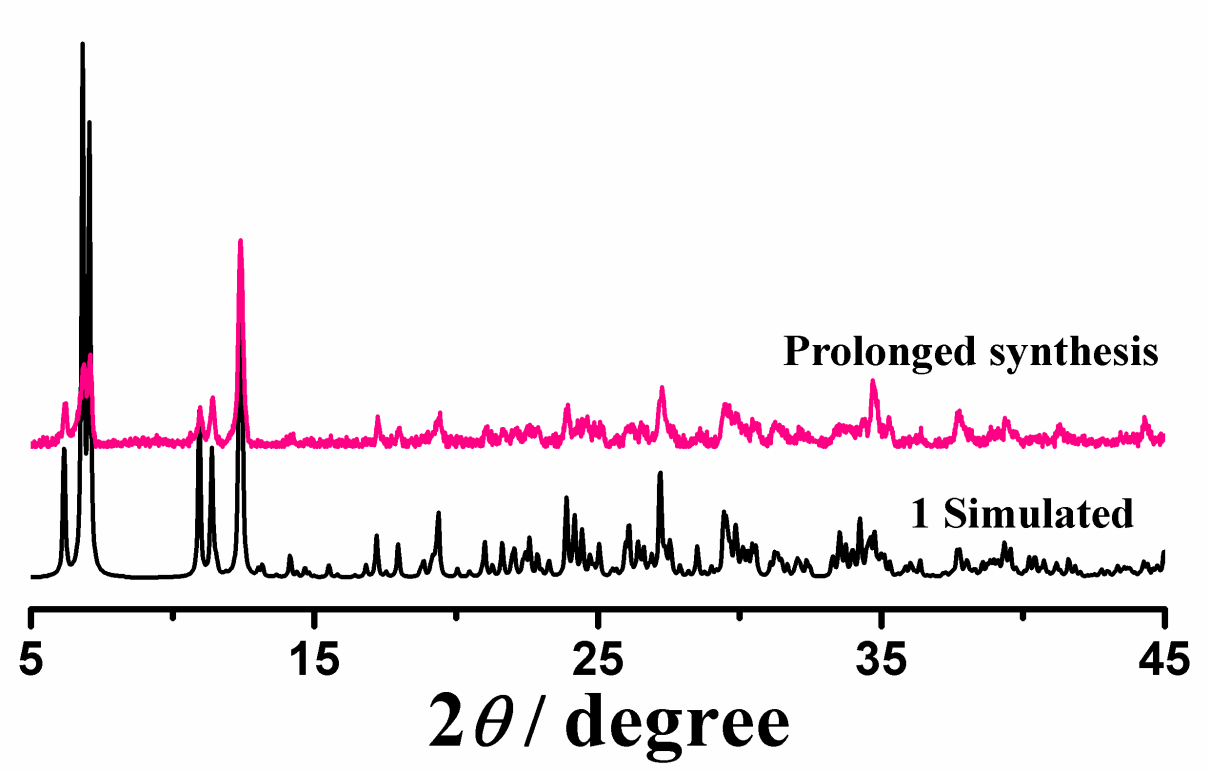

Fig. S14. The PXRD spectrum of prolonged synthesis.