

SUPPLEMENTARY INFORMATION

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Facile *in situ* formation of luminescent cellulose paper using Schweizer's reagent as an inorganic solvent in water

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CONTENT

EXPERIMENTAL

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FIG. S1 AND FIG. S2

EDX ANALYSIS

FIG. S3-S4 AND TABLE S1

NMR SPECTRA

FIG. S5-S7

Experimental

Characterisation

The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 298 K. Coupling constants (J) are reported in Hertz (Hz) and chemical shifts (δ) are reported in parts per million (ppm). ^1H spectra are referenced internally to residual proton impurity in the deuterated solvents (CD_3OD in all cases). Data is reported as resonance position (δH), multiplicity, assignment, and relative integral intensity. All the NMR data was processed and analysed using Bruker TopSpin 4.0.7 software. The melting points were determined with an Electrothermal IA9100 standard digital melting point apparatus. Photographs of the papers were captured using an Apple iPhone X mobile phone with a 12 MP (megapixel) wide-angle camera.

XRD measurements were obtained using a Bruker multi-purpose X-ray diffractometer D8-Avance operated in a continuous θ - θ scan in locked coupled mode with copper radiation. The sample was mounted in the centre of the sample holder on a glass slide and levelled up to the correct height. The measurements were obtained at a typical step size of 0.034° in 2θ . A position-sensitive detector, Lyn-Eye, was used to record diffraction data at a speed of 0.5 sec/step. The data was processed using EVA software from Bruker.

For SEM analysis, the samples were mounted onto aluminium stubs, using carbon tape. The samples were then gold coated thrice, using the Quorum Q150R ES rotary-pump coating system, in preparation for SEM imaging. SEM images were captured and EDX data was collected using a JEOL-JSM 7500F scanning electron microscope under high vacuum at an operating voltage of 15.0 kV.

Preparation of dithiophosphonic acid [HS₂P(4-C₆H₄OMe)(OCH₃)]

A 100 mL Schlenk tube was charged with [SP(S){4-C₆H₄OMe}]₂ (Lawesson's Reagent) (126 mg, 0.311 mmol). An excess amount of methanol (250 mg, 7.80 mmol) was added. The solution was stirred vigorously without heating. After approximately 20 minutes (or until the solution turned from cloudy white/yellow to clear), the reaction was complete. The dithiophosphonic acid was isolated as a viscous, clear liquid.

Preparation of Schweizer's reagent

In a flask, CuSO₄·5H₂O (77.6 mg, 0.311 mmol) was dissolved in water. In a separate beaker, KOH (34.9 mg, 0.622 mmol) was dissolved in water. The KOH solution was added to the CuSO₄·5H₂O solution with vigorous stirring, causing the dark blue solution to form a light blue precipitate. Ammonia gas was bubbled through the precipitate, with vigorous stirring, resulting in the formation of a dark blue solution, i.e. Schweizer's reagent.

Preparation of copper(I) cluster [Cu{S₂P(1,4-C₆H₄OMe)(OCH₃)}]₄

An amount of [HS₂P(4-C₆H₄OEt)(OCH₂CH₂CH₃)] (0.622 mmol) was added dropwise to the previously prepared solution of Schweizer's reagent (0.311 mmol), with vigorous stirring. The resulting yellow precipitate was collected by filtration and washed with deionised water, followed by washing with EtOH.

Preparation of paper 1 (F1)

An amount of the bacterial cellulose (BC) suspension (7.00 g, 0.311 mmol) was added to the previously prepared solution of Schweizer's reagent (0.311 mmol). An amount of [HS₂P(4-C₆H₄OEt)(OCH₂CH₂CH₃)] (0.622 mmol) was added dropwise to this solution, with vigorous stirring (see Video S1, ESI). The resulting mixture was dialysed against deionised water in a 5 L plastic beaker for 24 hours, using dialysis tubing cellulose membrane (MWCO 14,000). The dialysed mixture was dispensed into a plastic petri dish (diameter = 75 mm) and heated at 50 °C until dry.

Preparation of paper 2 (F2)

An amount of the BC suspension (7.00 g, 0.311 mmol) was combined with [Cu{S₂P(4-C₆H₄OEt)(OCH₂CH₃)}]₄ (92.3 mg, 77.8 μmol). The resulting mixture was sonicated for 45 minutes, using the Jeken PS-40A ultrasonic cleaner instrument. Thereafter, the mixture was dispensed into a plastic petri dish (diameter = 75 mm) and heated at 50 °C until dry.

Chemical data

[Cu{S₂P(1,4-C₆H₄OMe)(OCH₃)}]₄ The product was isolated as a pale yellow powder. Melting Point: the solid started to decompose at 159.8 °C to form a dark grey powder. ¹H NMR (400 MHz, CDCl₃): δ (ppm), J(Hz) 3.82 (s, CH₃, 3H), 3.84 (d, OCH₃, 3H, J_{P-H} = 14.36), 6.92 (dd, ArCH, 2H, J_{H-H} = 8.72, J_{P-H} = 3.08), 7.97 (dd, ArCH, 2H, J_{H-H} = 8.64, J_{P-H} = 13.56) ³¹P NMR (400 MHz, CDCl₃): δ (ppm) 92.47.

Photoluminescence testing

Photoluminescence spectra were recorded on a Perkin-Elmer LS-55 spectrometer equipped with a front surface accessory.

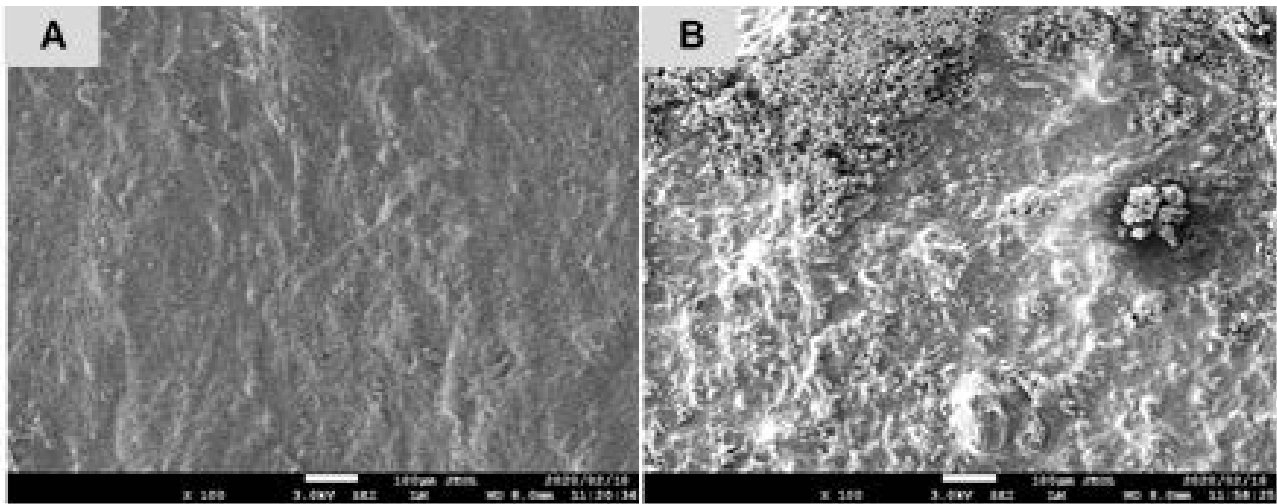


Fig. S1 Scanning electron micrographs of papers (A) F1 and (B) F2 at 100x magnification.

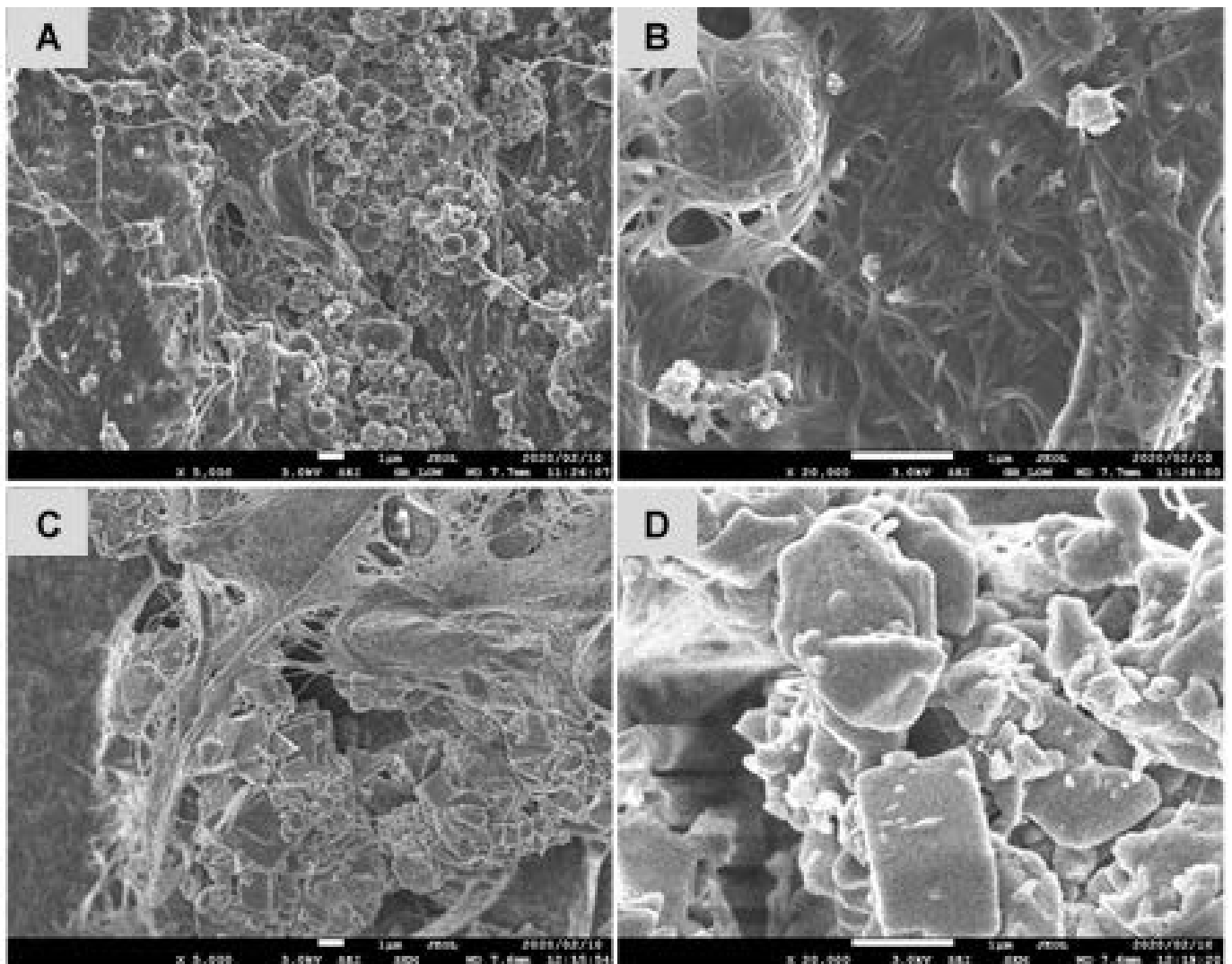


Fig. S2 Scanning electron micrographs of papers F1 (A) 5,000x (B) 20,000x magnification, and F2 (C) 5,000x (D) 20,000x magnification.

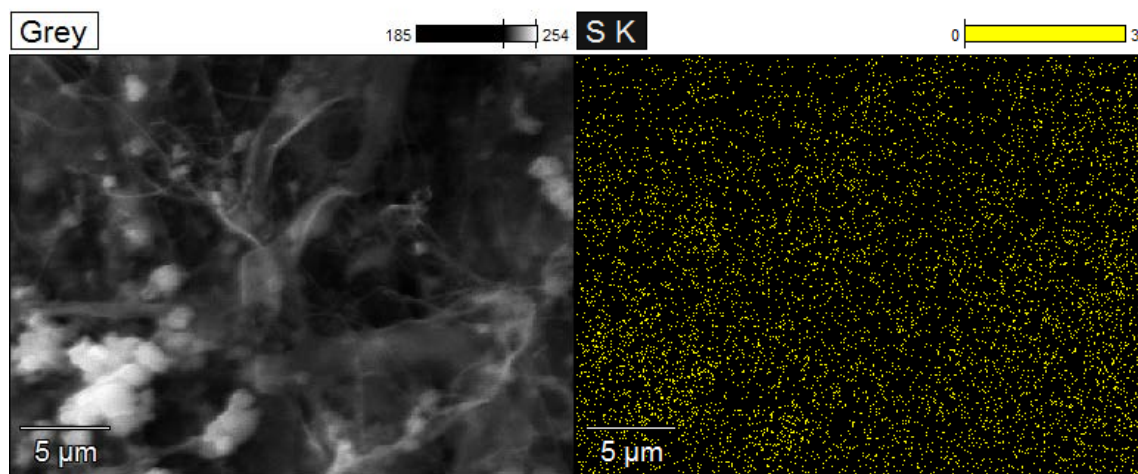


Fig. S3 (left) SEM micrograph and (right) EDX mapping of sulfur for F1.

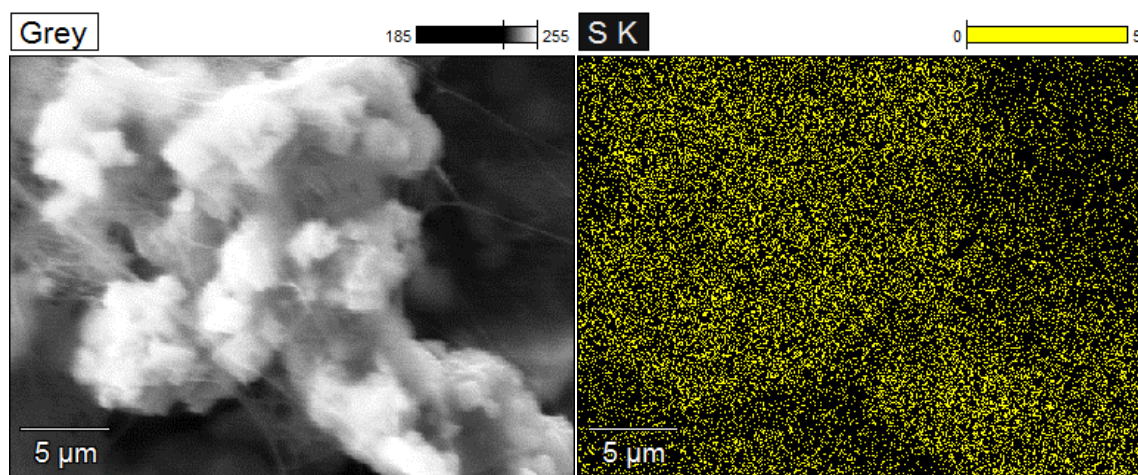


Fig. S4 (left) SEM micrograph and (right) EDX mapping of sulfur for F2.

Table S1 Surface elemental composition of F1 and F2.

	Weight percentage ^a (%)	
	F1	F2
C	46.6	65
O	32.5	18
P	4.1	5
S	9.0	6.8
Cu	7.8	5.2

^aObtained from EDX spectra of SEM micrographs.

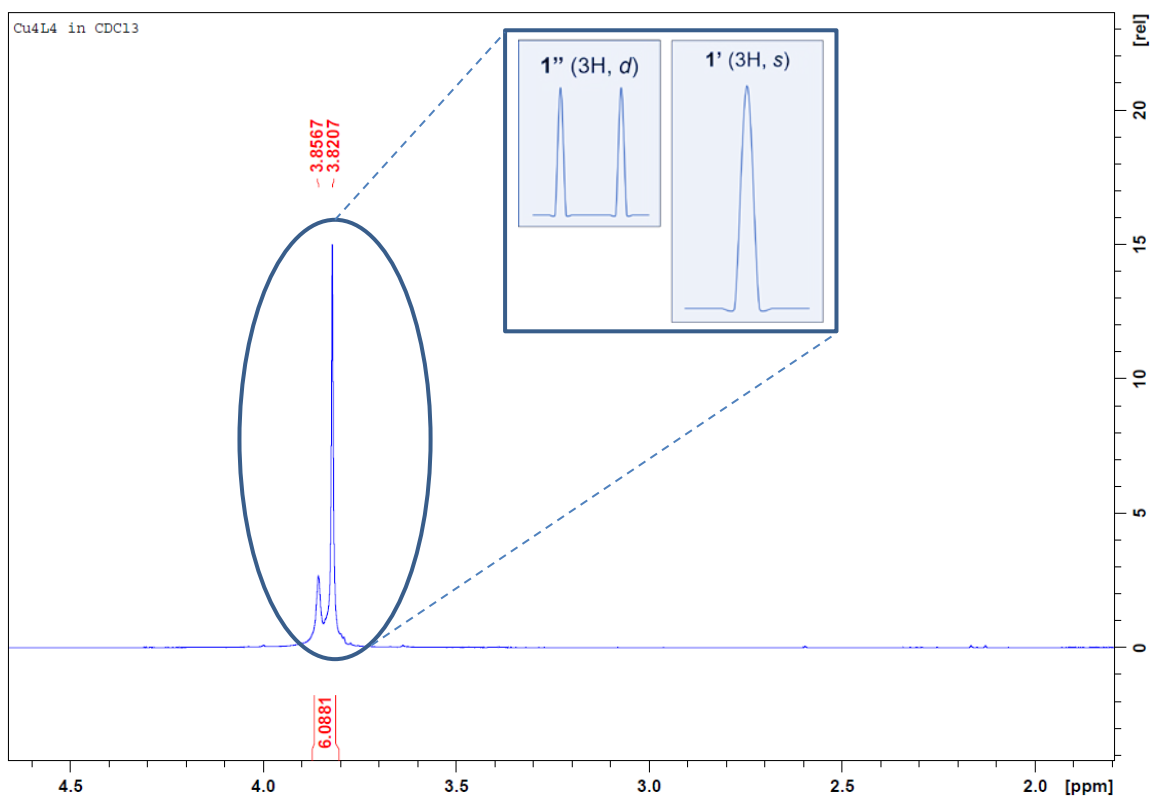


Fig. S5 Aliphatic region of ^1H NMR spectrum for $[\text{Cu}\{\text{S}_2\text{P}(1,4\text{-C}_6\text{H}_4\text{OMe})(\text{OCH}_3)\}]_4$.

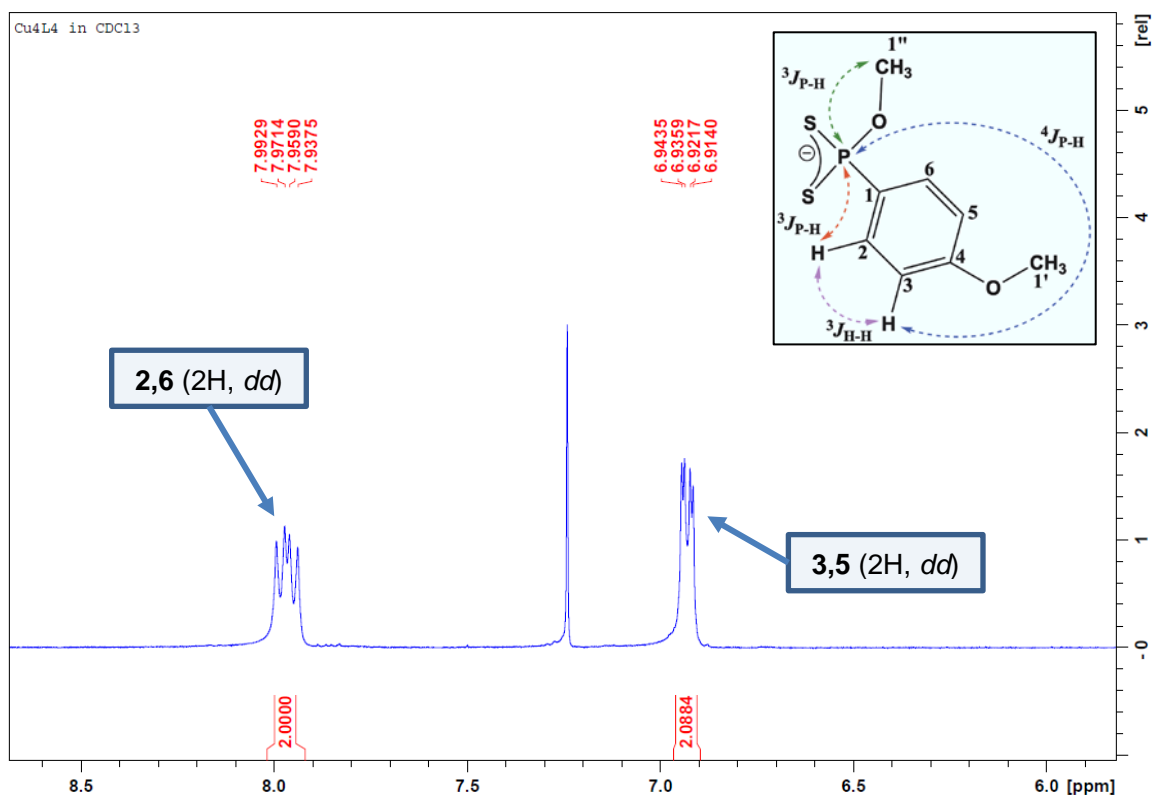


Fig. S6 Aromatic region of ^1H NMR spectrum for $[\text{Cu}\{\text{S}_2\text{P}(1,4\text{-C}_6\text{H}_4\text{OMe})(\text{OCH}_3)\}]_4$.

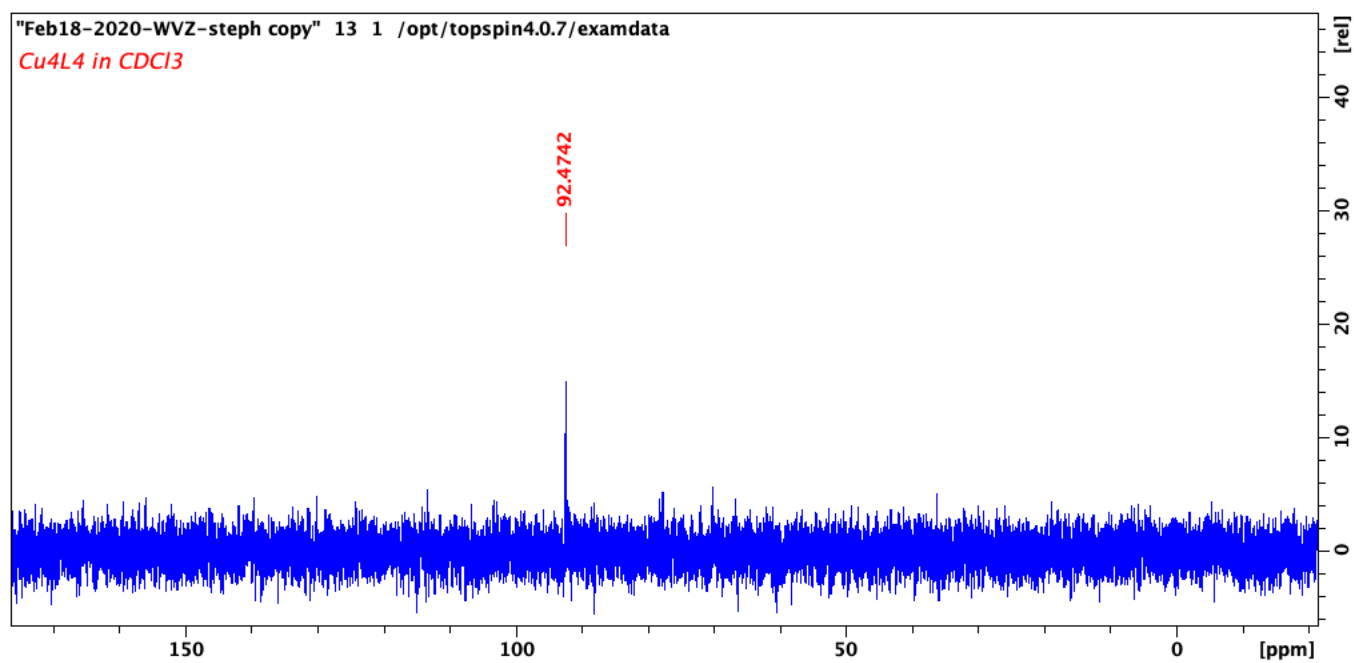


Fig. S7 ^{31}P NMR spectrum of $[\text{Cu}\{\text{S}_2\text{P}(1,4\text{-C}_6\text{H}_4\text{OMe})(\text{OCH}_3)\}]_4$.