A second sphere coordination adduct containing one-dimensional water/methanol channels: X-ray structures, thermal stability and single crystal impedance spectroscopy analysis.†‡

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Figure S12. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO immersed in $CHCl_3$ for 24 h. There is no presence of $CHCl_3$. ^{1} H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.33 (8H, m, ArH), 10.15 (6H, m, -NH_3^+).

Figure S13. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO immersed in CH_2Cl_2/$CHCl_3$ for 24 h. There is no presence of $CHCl_3$ but DCM. ^{1} H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.31 (8H, m, ArH), 10.15 (6H, m, -NH_3^+), 5.74 (0.1H, s, CH_2Cl_2).

Figure S14. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO immersed in THF for 24 h. There is no presence of THF. ^{1} H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.34 (8H, m, ArH), 10.14 (6H, m, -NH_3^+).

Figure S15. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO immersed in toluene for 24 h. There is no presence of toluene. ^{1} H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.33 (8H, m, ArH), 10.13 (6H, m, -NH_3^+).

Figure S16. Experimental treatment of **1** before impedance spectroscopy. Top right view of the single crystals in the vial. Bottom, view of the gold interdigitated electrodes used to perform the impedance measurements.

Figure S17. Nyquist plot of **1** measured at room temperature in the orientation 4.

Figure S18. Impedance spectroscopy measured after calibration (black), with only the electrodes (red) and with electrodes covered with protectant oil (blue).

Figure S19. Impedance spectroscopy of a second crystal of **1** measured in orientation 1 after at different times.

Figure S20. Conductivities of a new crystal **1** measured at different times.

Figure S21. Impedance spectroscopy measured for only the electrodes (black) and after heating a crystal of **1**.

Figure S22. Images of a single crystal of **1** oriented with the channels parallel to the FET (10 μm long channel). Images of the same single crystal after heating to 110°C for 10 minutes. Image showing the single crystal after being removed from the FET after measuring AC impedance spectroscopy in the orientation 1 shown in Figure S11.

Figure S23. Face indexing of a crystal of **1** (not the same as the one shown in Figure 3 as it was too big to measure single crystal X-ray for indexing). Clearly, the *a*-axis extends perpendicular to the largest faces of **1**.

Figure S24. Cartoon showing the relative orientation between the electrodes and the 1D channels when the channels are parallel to the gold electrodes.

Experimental Details

Synthesis of 1.

A solution of 70 mg (0.35 mmol) **L** (4,4'- Diaminodiphenylmethane), 3ml MeOH and 6 drops of concentrated hydrochloric acid (about 0.3 mL) was placed in a 25 ml Erlenmeyer flask, then 120 mg (0.70 mmol) $CuCl_2$•$2H_2O$ were added. The flask was shaken until the contents were completely dissolved. The flask was allowed to stand for 4–5 days at room temperature and gave yellow block crystals of **1**. M.p. 220–235 °C.

Guest removal and inclusion experiments in 1.

Guest inclusion on an evacuated channel using powder samples: Single crystals of **1**were picked up the from the mother solution (methanol), and used a filter paper to clean the crystals until they were dry. Then we ground the crystals into crystalline powders. The powder samples were heated at 160 °C for 2h. After that, we accurately weigh 10 mg of the heated sample and put them into an erlenmeyer flask with 3ml dichloromethane. The same weight of the heated sample was also put inside chloroform, tetrahydrofuran, toluene and dichloromethane/chloroform, respectively. The flasks were covered and left them at room temperature. After 24 hours, we picked out the samples from the solvents, and used filter paper to clean until they all dry enough. We noted that there was no much change of the crystalline sample before and after putting them into the solvents.

We have used ^{1}H NMR to test the sample employing dimethyl sulfoxide-d6 to dissolve the crystals to analyze the guest exchange process. The ^{1}H NMR experiments were carried out on Mercury−Vx−300M Nuclear Magnetic Resonance instrument.

Guest inclusion on an evacuated channel using single crystals: We have also attempted to obtain a single crystal structure of **1** including DCM (i.e. **1•DCM**). Single crystals of **1** were heated to 160 °C for 2 hours and immediately immersed in DCM for 48 hours. Clearly the crystal observed under optical microscope showed that cracks developed forming an orthogonal grid in a parallelepiped shape. However, a small piece of crystal was obtained from the parent crystal and mounted for single crystal X-ray diffraction. We note that due to the small crystal size and the increase in mosaisicity the X-ray data was only possible to be collected up to 1 Å resolution. Indexing of the unit cell gave slightly different cell parameters but the same space group (Figure S8). Crystal structure determination revealed

that the framework is maintained but now the channels are filled with DCM molecules which are disordered in two positions (Figure S8 and S9).

1

Figure S1. Actual single crystal of **1**.

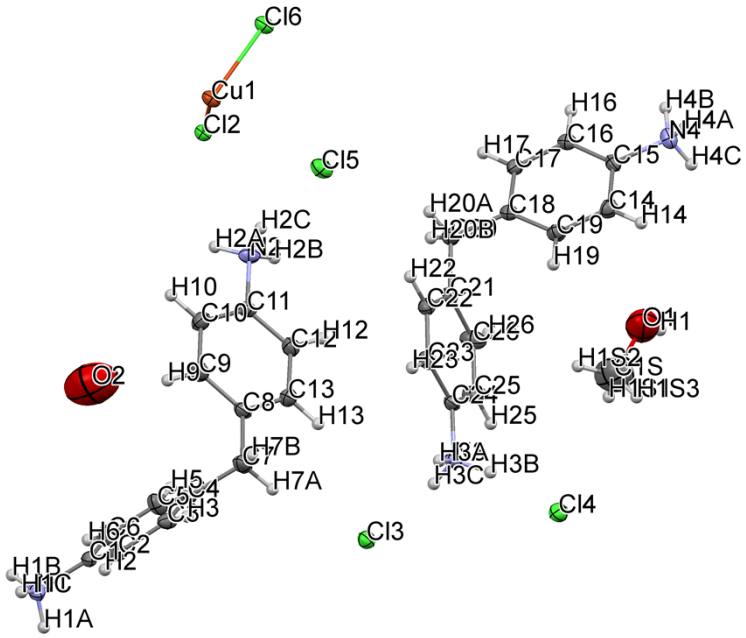


Figure S2. Asymmetric unit in **1.**

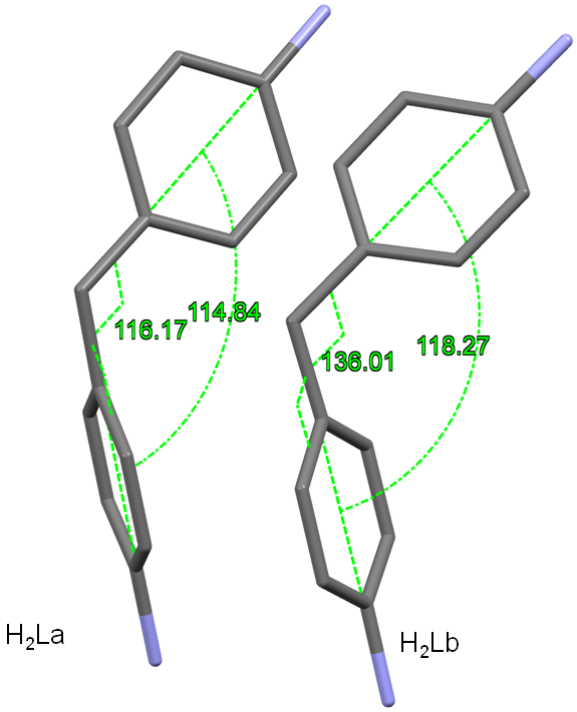


Figure S3. View of the torsion angles and the bent angle between the phenyl rings in each dication in **1**.

Table S1. Charge assisted hydrogen bonding interactions between dication $[H_2L]^{2+}$, dianion $[CuCl_6]^{4-}$ and Cl^-.

Interaction	D	H	A	D···A(Å)	D–H···A (°)
1	N4	H4C	Cl4	3.104(3)	165.8(2)
2	N4	H4B	Cl3	3.273(3)	152.3(2)
3	N4	H4A	Cl6	3.241(3)	152.9(2)
4	N3	H3C	Cl3	3.207(3)	166.7(2)
5	N3	H3A	Cl5	3.119(3)	170.6(2)
6	N2	H2A	Cl4	3.221(2)	148.2(2)
7	N2	H2B	Cl3	3.213(3)	167.3(2)
8	N2	H2C	Cl5	3.189(3)	158.3(2)
9	N1	H1B	Cl4	3.190(3)	162.4(2)
10	N1	H1C	Cl2	3.152(2)	111.3(2)
11	N1	H1A	Cl3	3.306(3)	164.1(2)

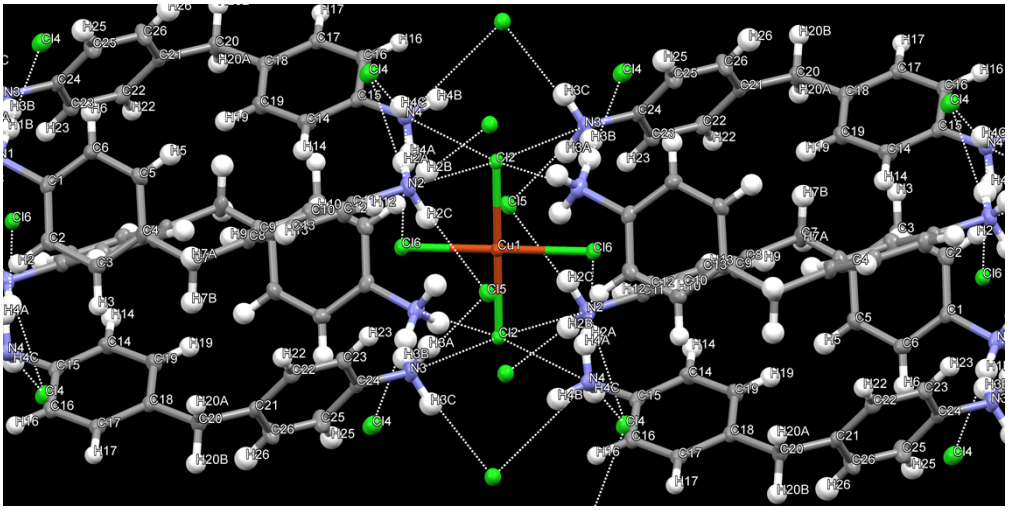


Figure S4. Detailed view of the charge assisted hydrogen bonding interactions in involving $[CuCl_6]^{4-}$, Cl^- and H_2L dication in **1**. For a clearer view and analysis, see the CIF.

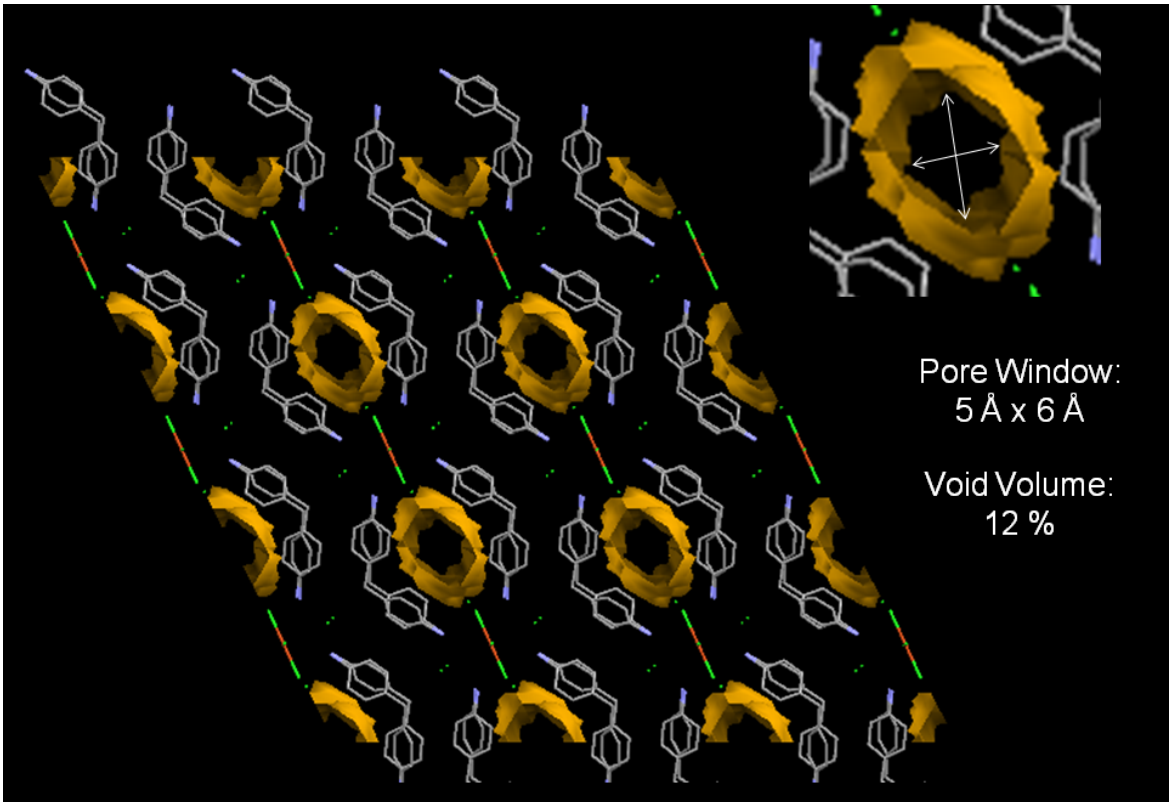


Figure S5. Voids in **1** viewed along the *a*-axis observed after manually removing water and methanol guest molecules.

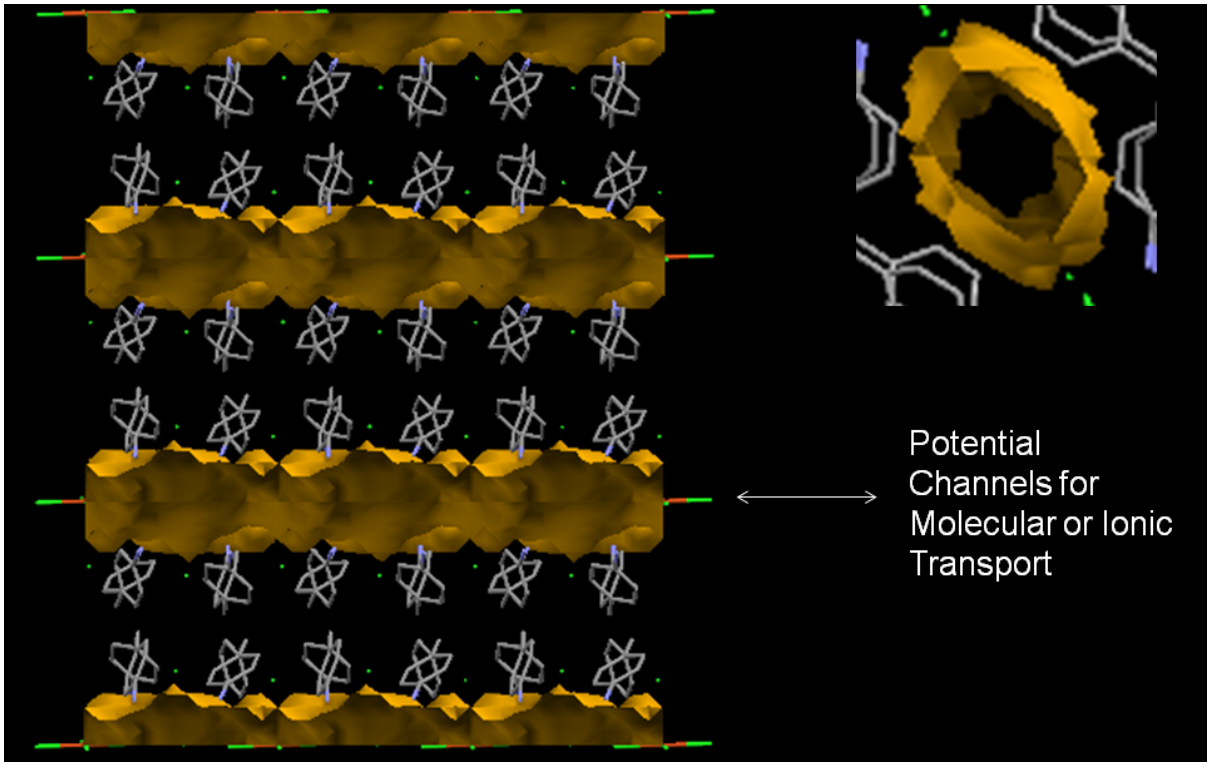


Figure S6. Voids in **1** viewed along the *c*-axis observed after manually removing water and methanol guest molecules.

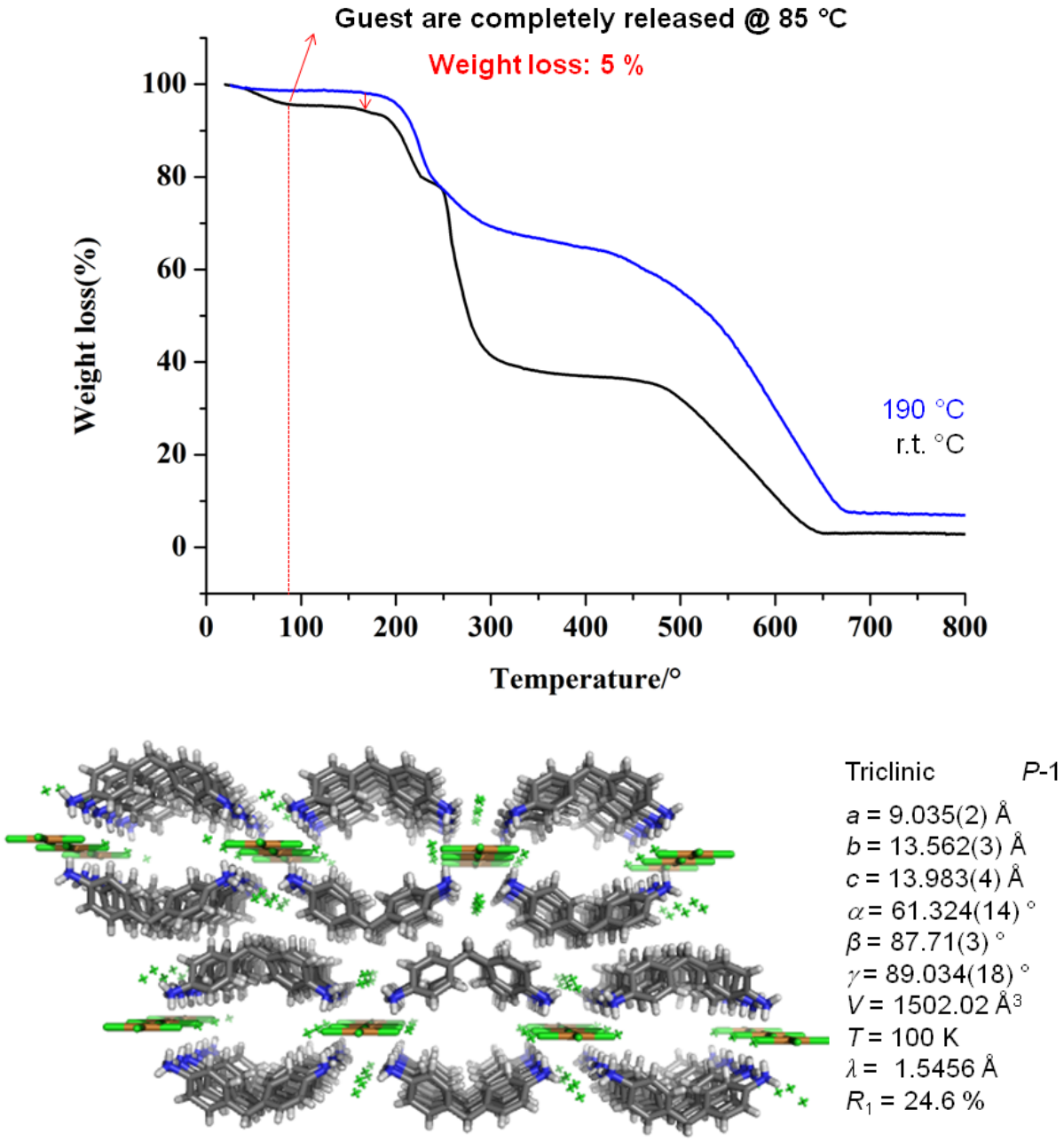
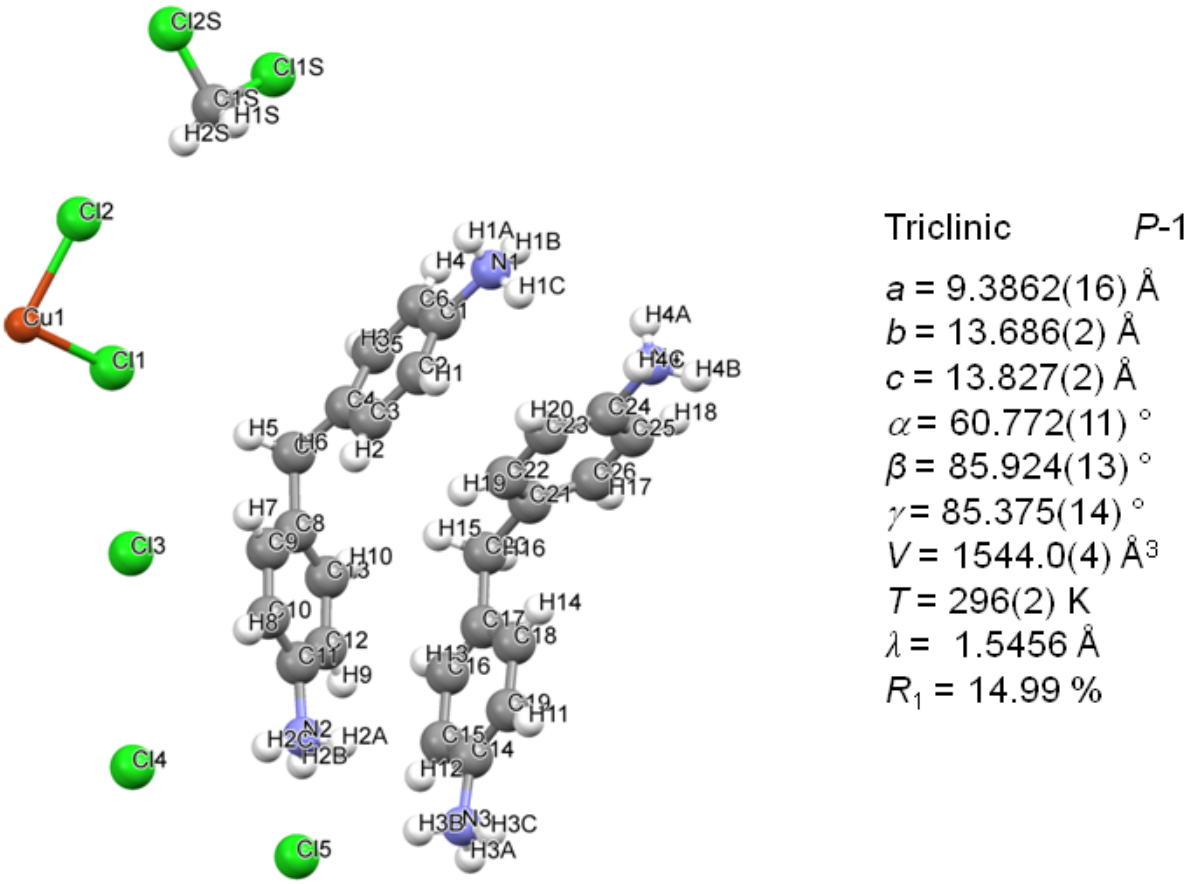


Figure S7. TG plot of **1** (black line) and **1** after being heated to 190 °C (blue) (top). View along the *a*-axis of the crystal structure obtained after heating **1** up to 160 °C recorded at 100 K. The same topology as the as synthesized **1** is maintained (bottom).



Triclinic *P*-1

a = 9.3862(16) Å
b = 13.686(2) Å
c = 13.827(2) Å
α = 60.772(11) °
β = 85.924(13) °
γ = 85.375(14) °
V = 1544.0(4) Å^3
T = 296(2) K
λ = 1.5456 Å
R_1 = 14.99 %

Figure S8. Asymmetric unit in **1•DCM.** Only one of the two disordered DCM molecules are shown in the assymetric unit.

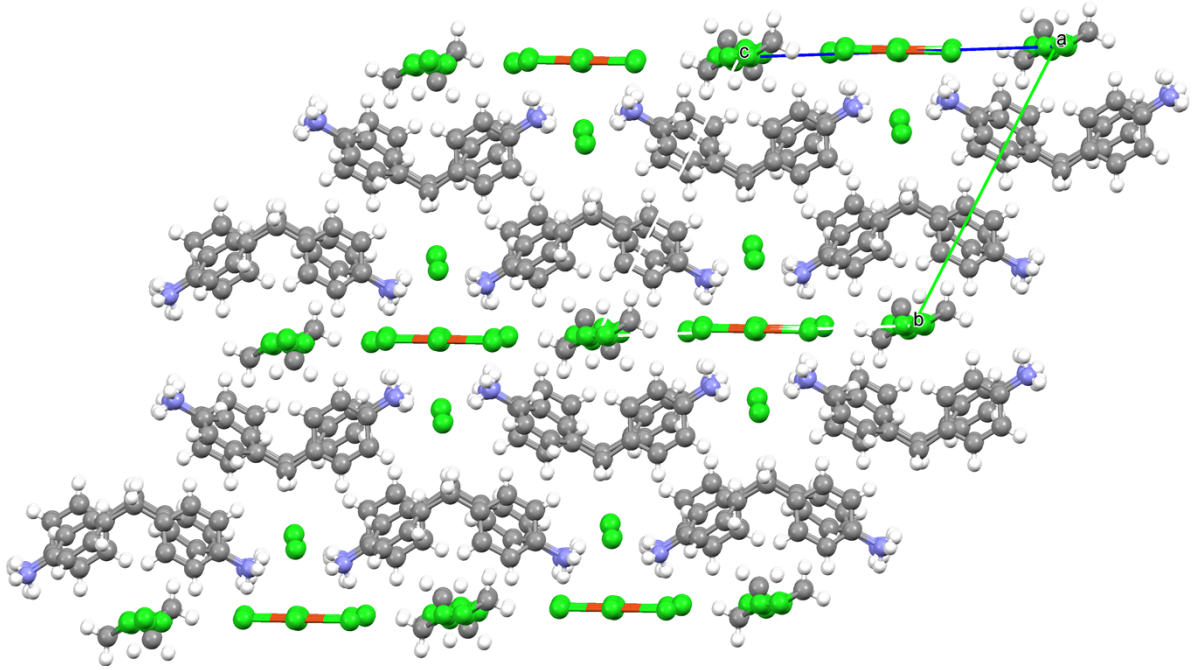


Figure S9. Crystal packing viewed along the *a*-axis in **1•DCM.** For further details see the CIF file associated.

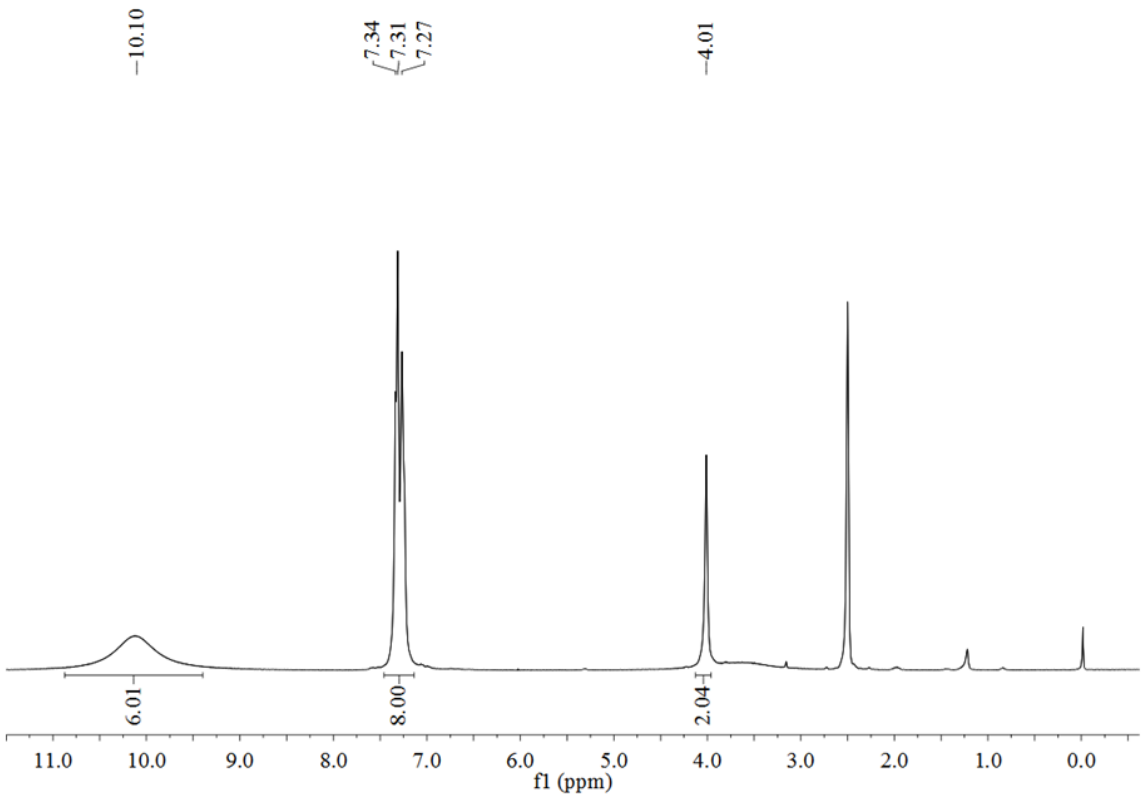


Figure S10. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO. ^{1}H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.34 (8H, m, ArH), 10.10 (6H, m, -NH_3^+).

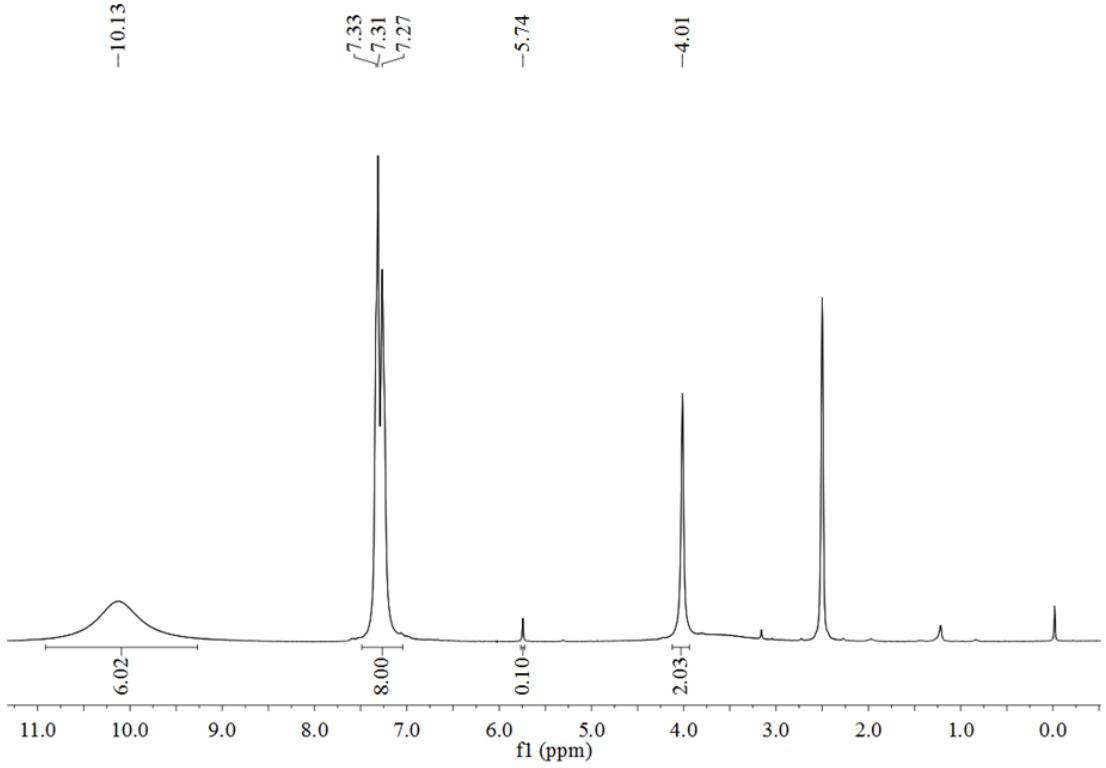
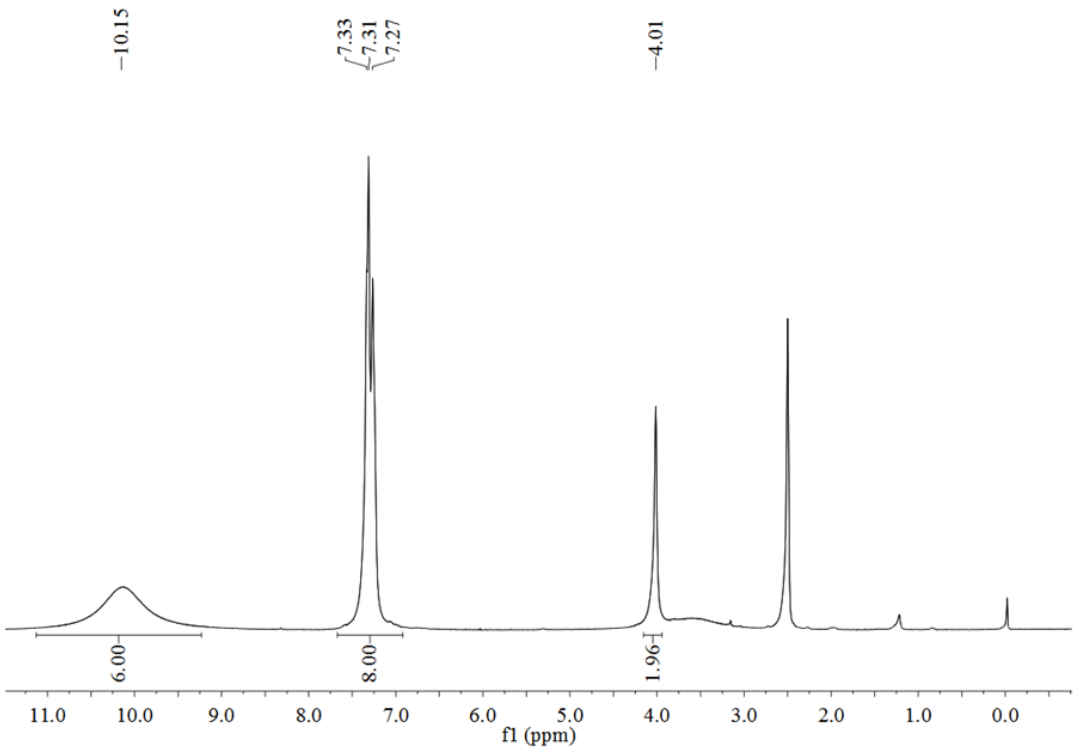


Figure S11. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO and immersed in DCM for 24,. The presence of DCM is evident from the peak at 5.74. ^{1}H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.33 (8H, m, ArH), 10.13 (6H, m, -NH_3^+), 5.74 (0.1H, s, CH_2Cl_2).



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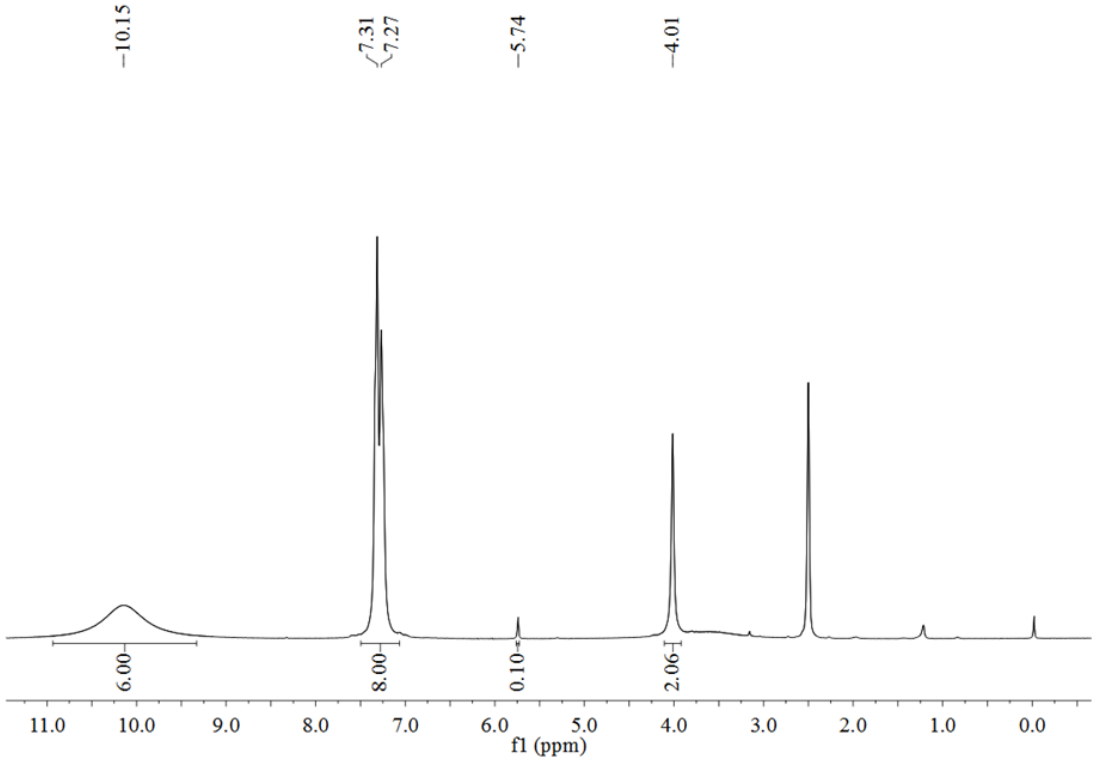

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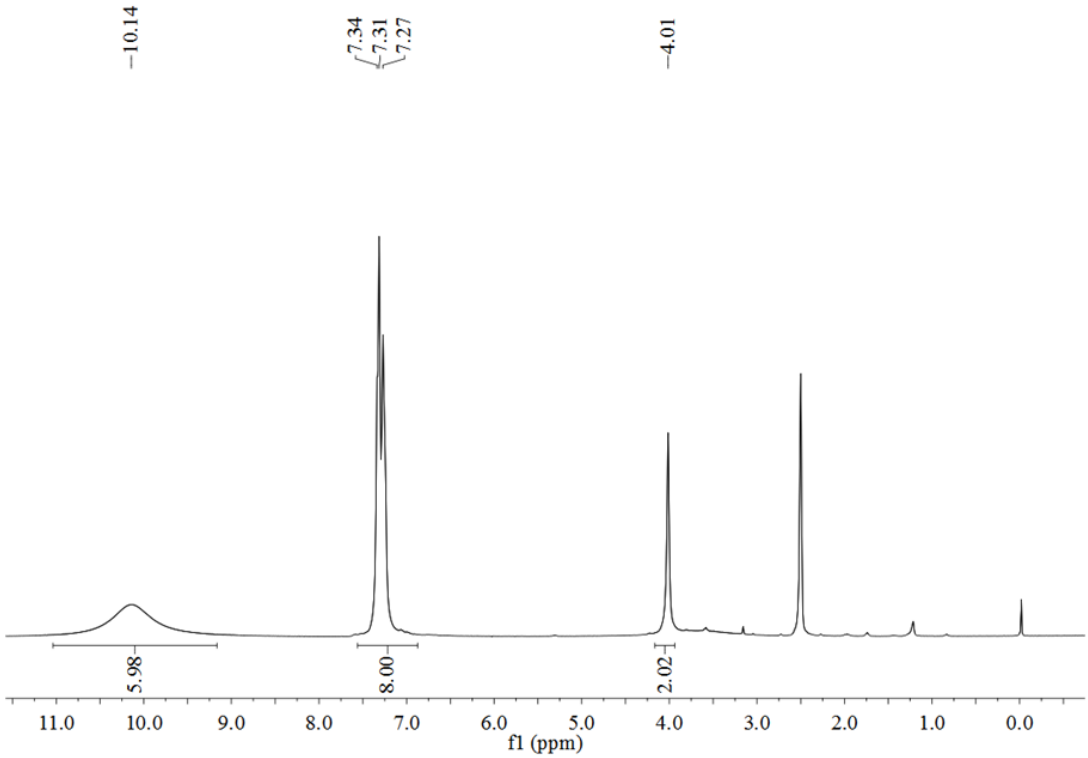

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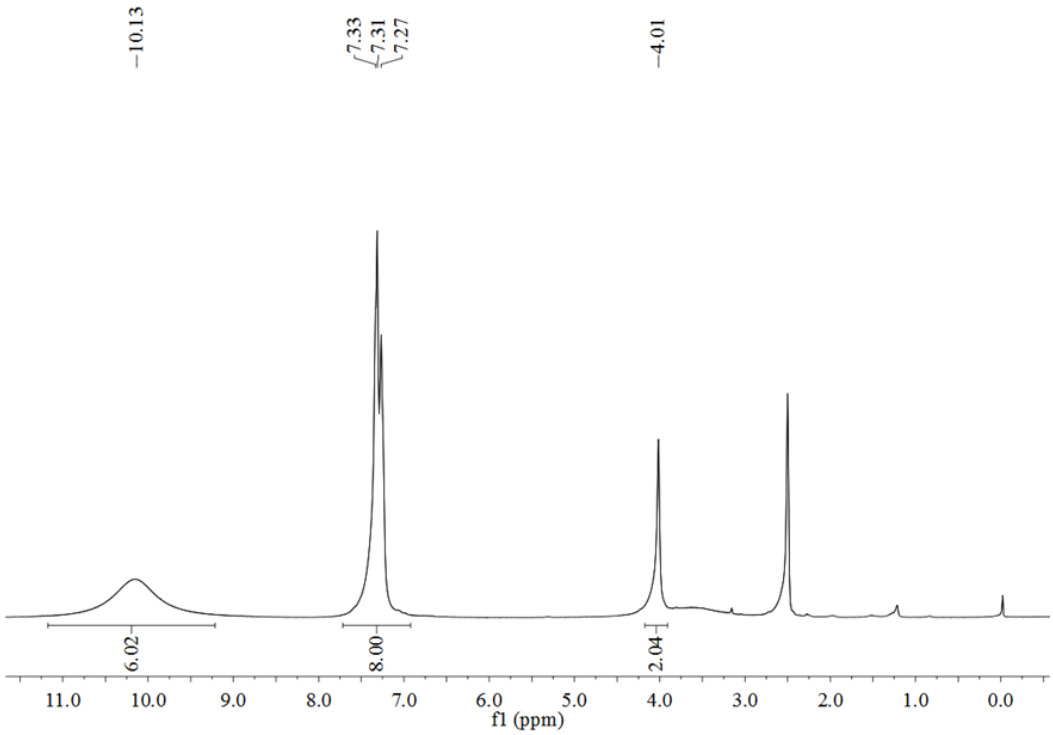
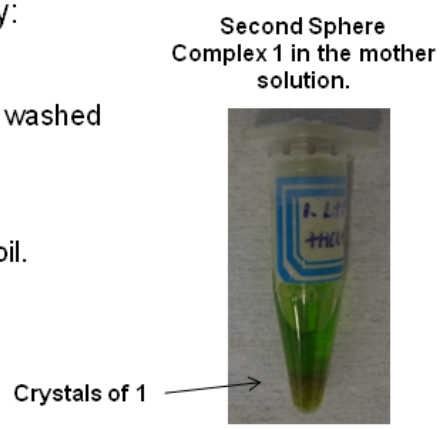


Figure S15. ^{1}H NMR spectra of **1** heated to 160 °C in DMSO immersed in toluene for 24 h. There is no presence of toluene. ^{1} H NMR (DMSO, 300 MHz) δ: 4.01 (2H, s, -CH_2), 7.27-7.33 (8H, m, ArH), 10.13 (6H, m, -NH_3^+).

Treatment of **1** before the impedance spectroscopy:

i) The crystal was removed from the mother solution and washed with $CHCl_3$.
ii) Then it was immersed in mineral oil.
iii) Then washed with hexane to remove the oil film.
iv) Then the crystal was covered with thin film of mineral oil.
v) The process is repeated three times.



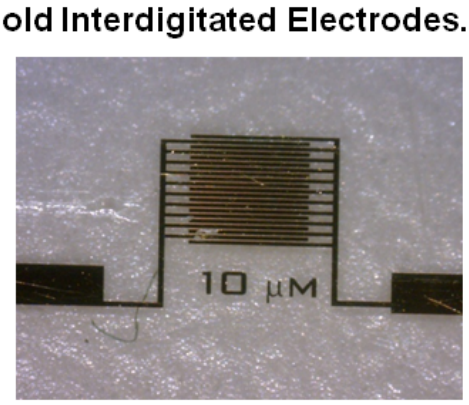


Figure S16. Experimental treatment of **1** before impedance spectroscopy. Top right view of the single crystals in the vial. Bottom, view of the gold interdigitated electrodes used to perform the impedance measurements.

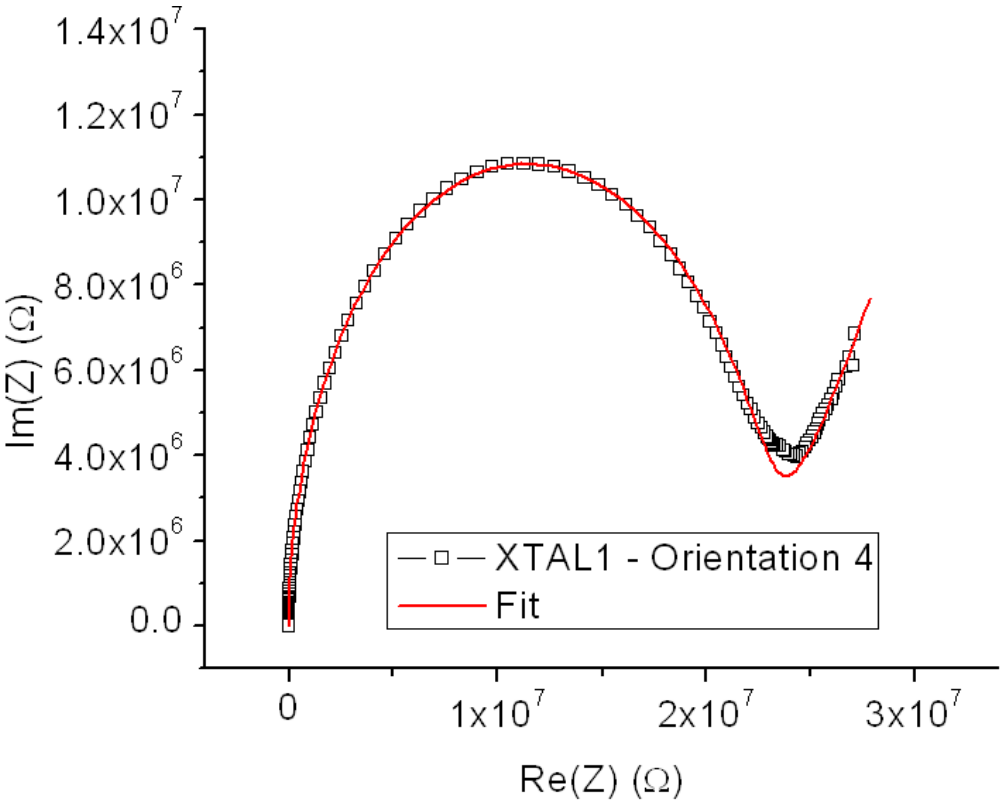


Figure S17. Nyquist plot of **1** measured at room temperature in the orientation 4.

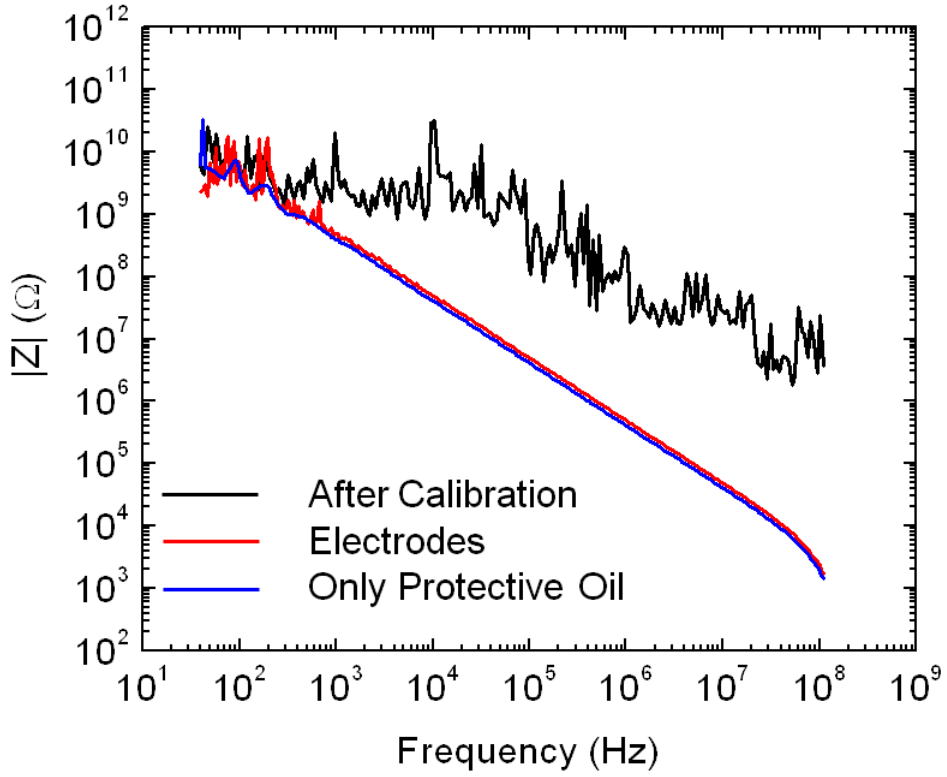


Figure S18. Impedance spectroscopy measured after calibration (black), with only the electrodes (red) and with electrodes covered with protectant oil (blue).

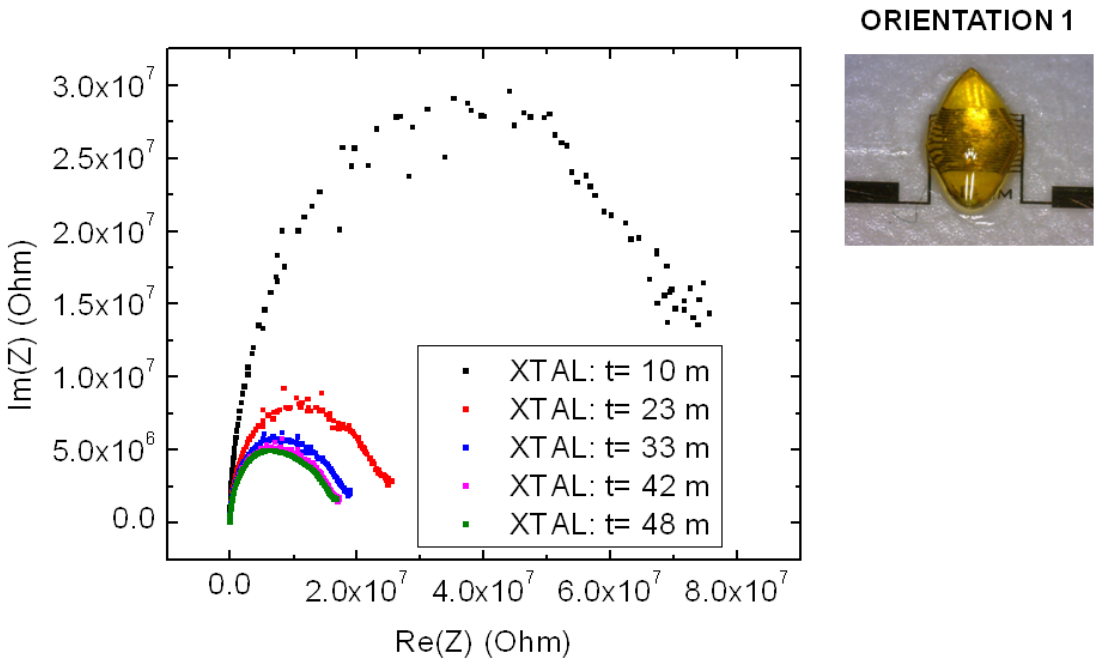


Figure S19. Impedance spectroscopy of a second crystal of **1** measured in orientation 1 after at different times.

Orientation 1

Time (min)	Conductivity (S cm^{-1})
0	N/A
10	3.77E-10
23	1.10E-09
33	1.53E-09
42	1.68E-09
48	1.74E-09

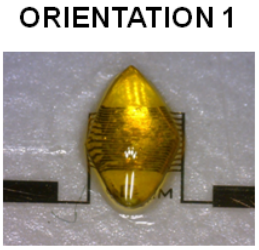


Figure S20. Conductivities of a new crystal **1** measured at different times.

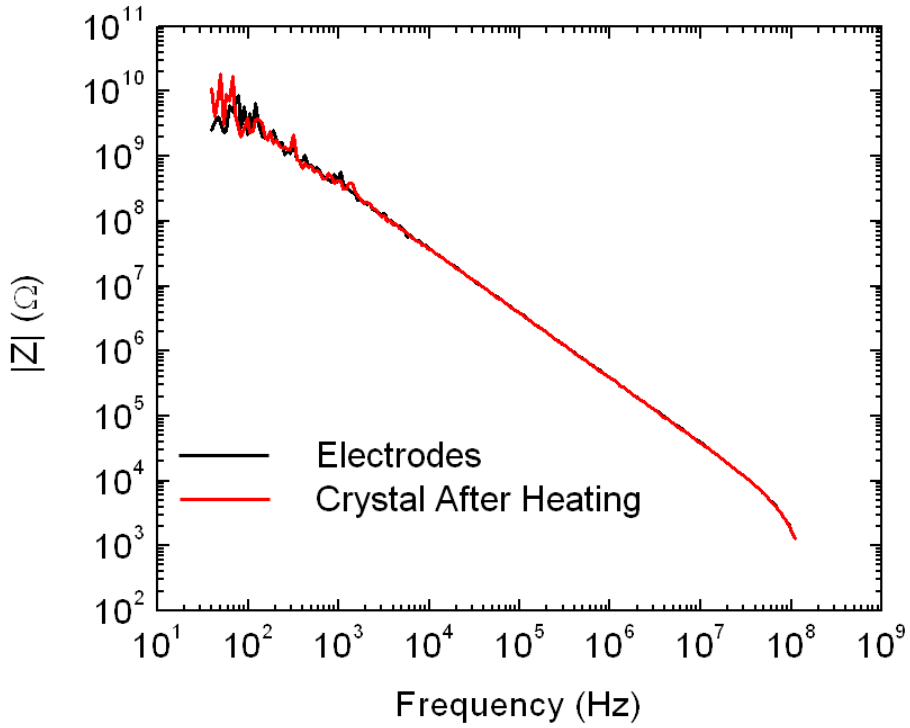


Figure S21. Impedance spectroscopy measured for only the electrodes (black) and after heating a crystal of **1**.

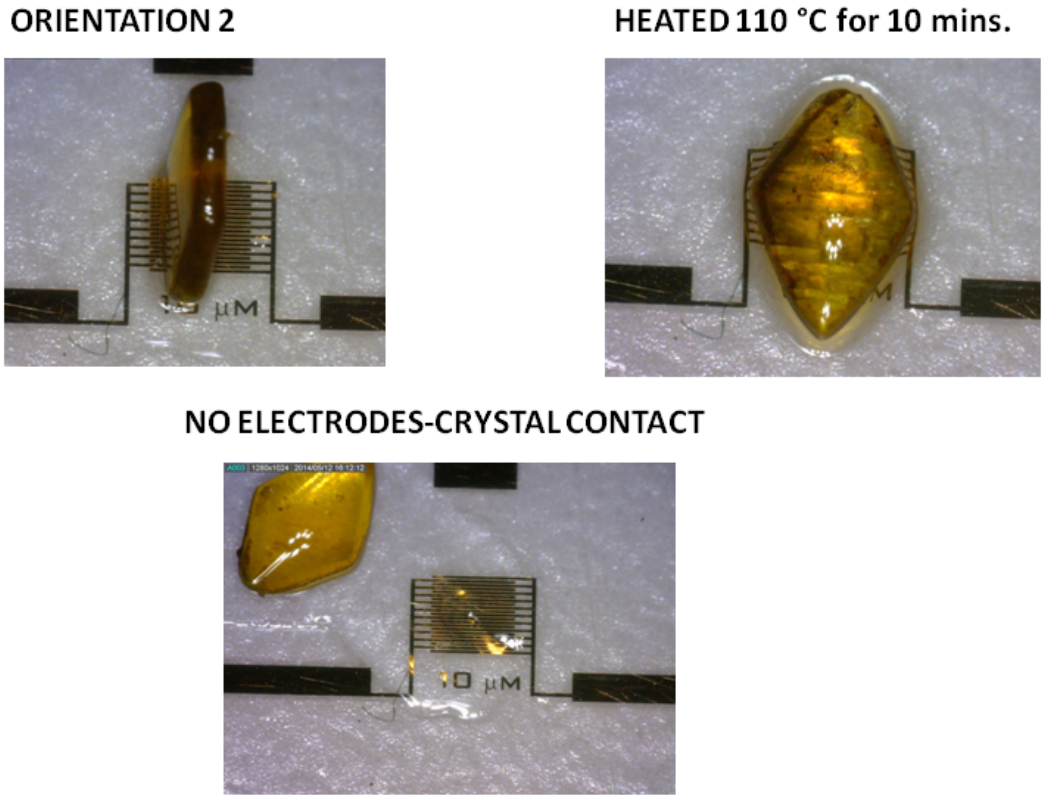


Figure S22. Images of a single crystal of **1** oriented with the channels parallel to the electrodes (10 μm long channel). Images of the same single crystal after heating to 110°C for 10 minutes. Image showing the single crystal after being removed from the electrodes after measuring impedance spectroscopy in the orientation 1 shown in Figure S11.

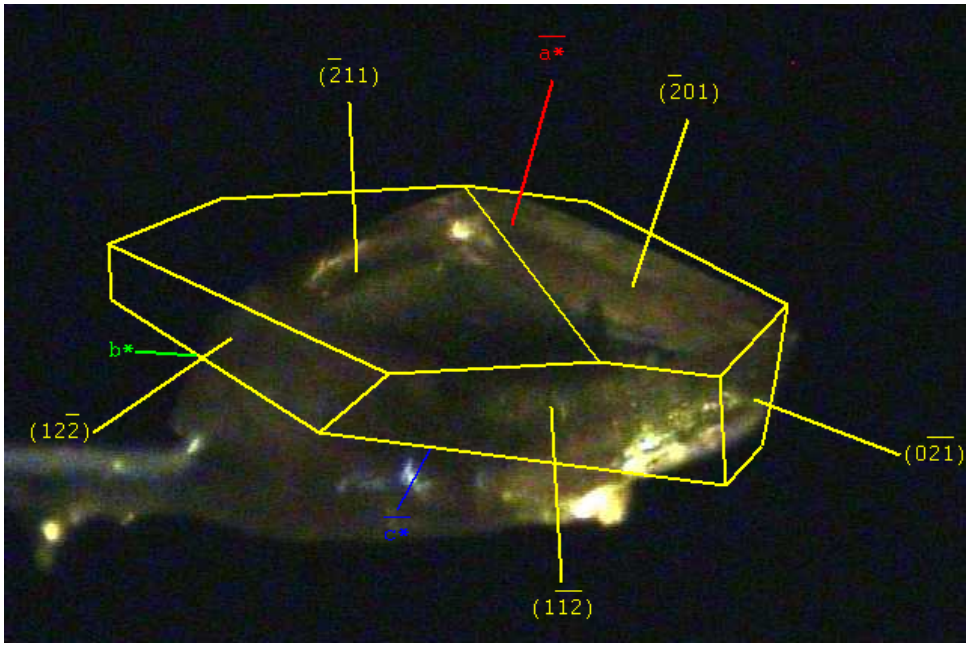


Figure S23. Face indexing of a crystal of **1** (not the same as the one shown in Figure 3 as it was too big to measure single crystal X-ray for indexing). Clearly, the *a*-axis extends perpendicular tot he largest faces of 1.

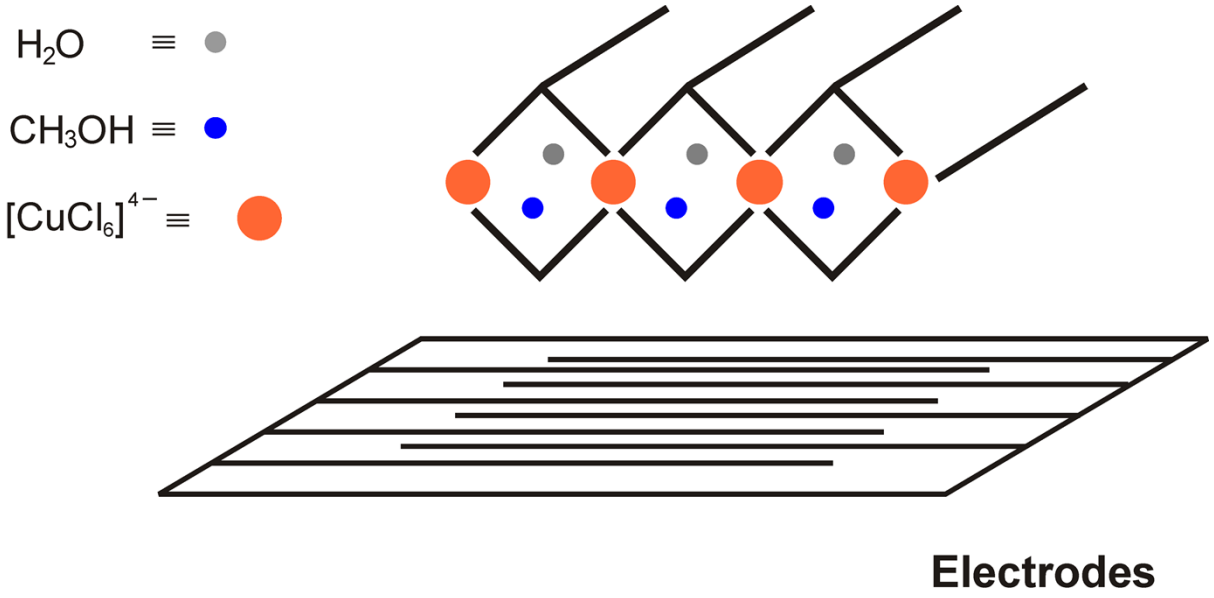


Figure S24. Cartoon showing the relative orientation between the electrodes and the 1D channels when the channels are parallel tot he gold electrodes.