

Supporting Information for

Dual mechanoluminescence system comprising a solid-state di-copper (I) complex containing *N*-heterocyclic carbene ligands

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1) Determination of solvation state of complex **1** solid

The spectra in Fig. S1 indicate the presence of acetone in the initial sample and the solvation-free states of solids **A** and **B**. In addition, other proton signals located at the same chemical shift for each sample, showing that the geometry of the dissolved states of complex **1** was identical, despite of the distinct difference in the solid states prior to dissolution in DMSO-*d*₆.

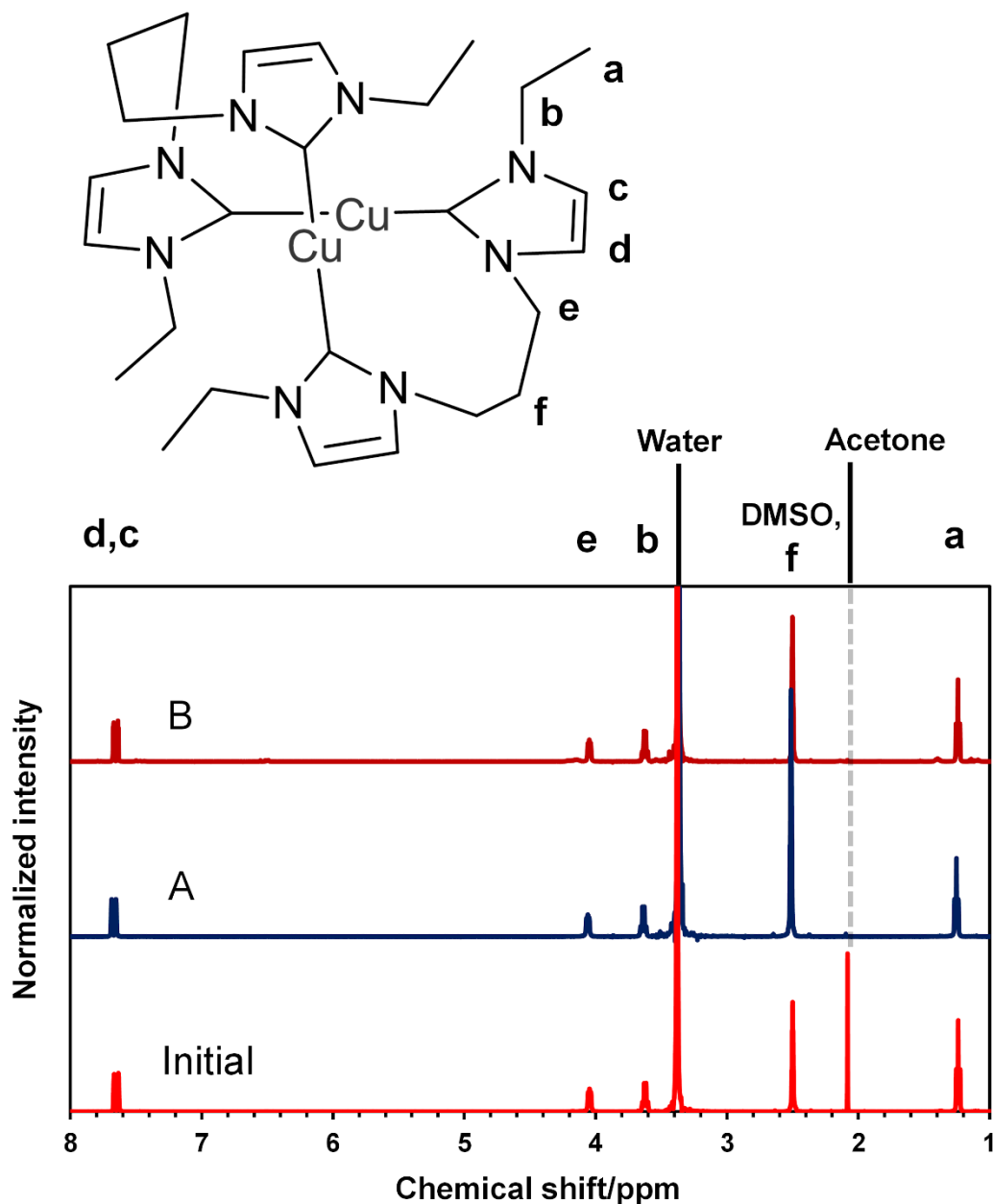


Figure S1 ¹H-NMR spectra obtained by dissolving various complex **1** states in DMSO-*d*₆. The initial state was the as-synthesised sample. Solid **A** was obtained by heating the initial sample to 130 °C. Solid **B** was obtained by mechanically grinding and heating solid **A** to 180 °C.

Figure S2 shows the desolvation behaviour of acetone from the initial solid (as-synthesised; **AS**) and solid (**ASG**) obtained by grinding the **AS**. The mass reduction ratio for **AS** was 5.7 wt%, confirming that the acetone in the initial solid was removed by heating. This was in accord with the result of the single-crystal X-ray structure analysis.^{S1} However, both the desolvation temperature and reduction rate of **ASG** decreased compared to those of **AS**. Therefore, it was determined that grinding modified the solid state. Highly pure, solvent-free solid **A** was obtained after the desolvation of **ASG**. No mass reduction was observed in solid **A**.

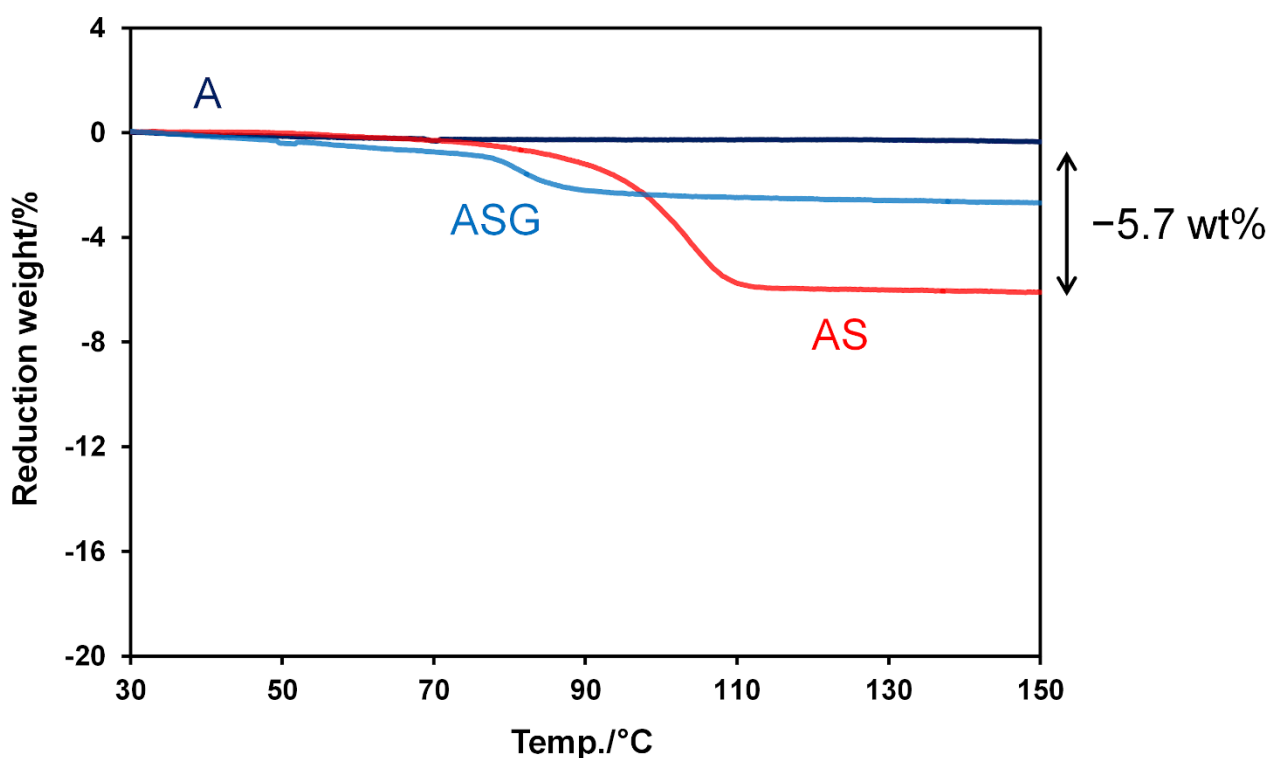


Figure S2 TG analysis of complex **1** solids. The initial state was as-synthesised sample, **AS**. **ASG** was obtained by grinding **AS**. Solid **A** was obtained by heating **ASG** to 130 °C.

2) Photophysical properties of complex **1** in powder state

Figure S3 shows the results of lifetime measurements for each solid. Deviation from the linear curves was observed for each result, suggesting that at least two kinds of emissions occurred. The optimisation of the fitting curves combining two types of emission resulted in the best fit.

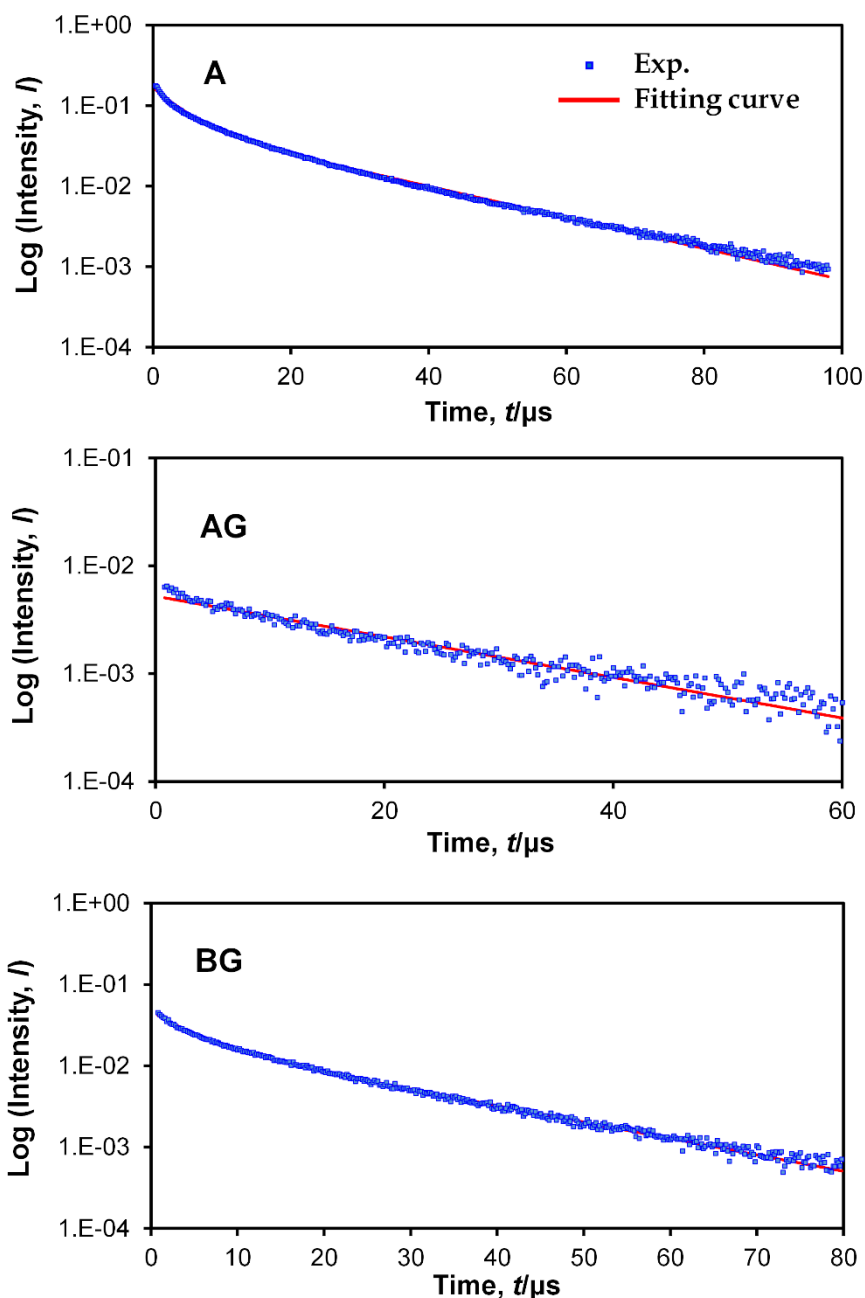


Figure S3 Lifetime measurement of photo-luminescence of complex **1** solids.

As shown in Table S1, the lifetime of the main emissions was approximately 23 μ s for every solid, suggesting that the species emitted must be similar.

Table S1 Photophysical properties of the complex 1 solid in powder states. The second term of the lifetime (τ_2) values for the emission is shown in parentheses.

Solid	$\lambda_{em,max}$ / nm	τ^* / μ s	Φ / %
A	510	22.5, (4.28)	61
AG	520	25.4, (0.12)	35
BG	546	21.6, (4.50)	31

*The lifetime was estimated by optimising the following fitting equation (1):

$$I = I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

where I_1 and I_2 are constant values and τ_1 and τ_2 are the corresponding lifetimes.

3) Supporting PXRD profiles of complex 1

As shown in Fig. S4a and b, the broadening of the diffraction peaks occurred in the spectra of both solid **A** and **B** after grinding.

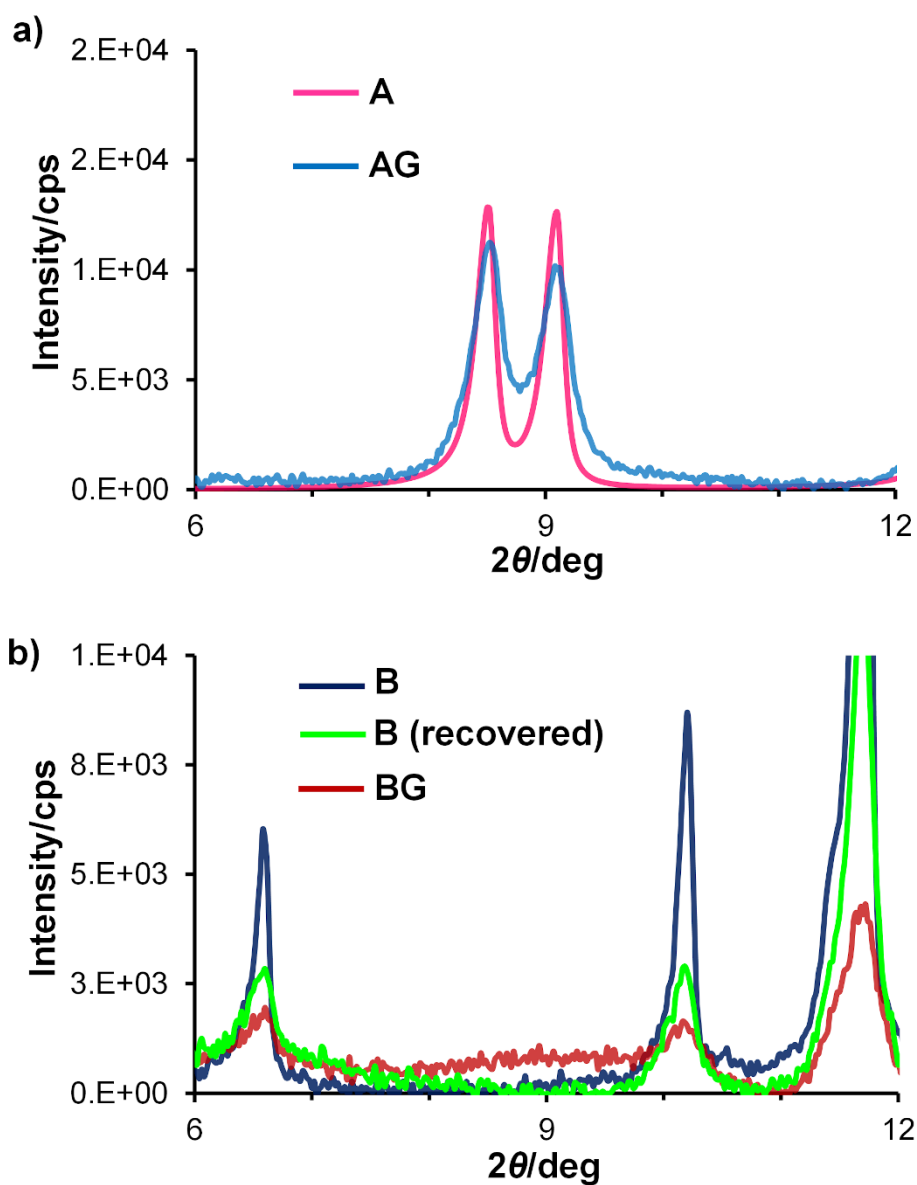


Figure S4 Enlarged PXRD profiles between 6 and 12° for (a) **A** and **AG**, and (b) **B**, **BG** and recovered **B** by heating..

4) Characterisation of di-silver (I) complex **2** [Ag₂(LEt)₂](PF₆)₂

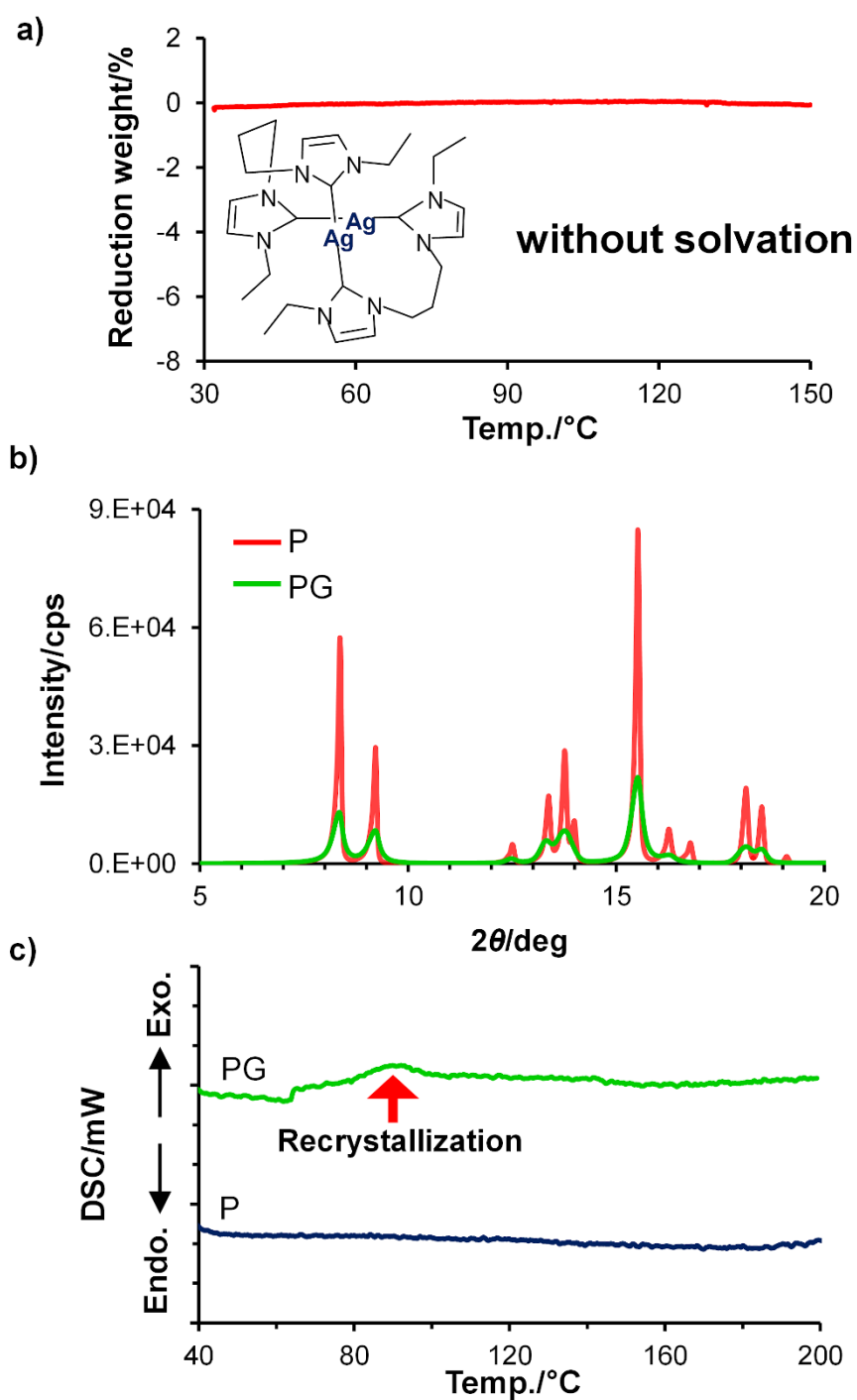


Figure S5 Characterisation of the di-silver (I) complex in the solid state. (a) TG analysis for **P**, (b) PXRD profiles, and (c) DSC heating thermograms for **P** and **PG**. **P** was obtained by precipitation in a diethyl ether/acetone solution and **PG** was obtained by grinding **P**.

Figure S5a shows the TG analysis for the di-silver (I) complex solid, **P**, which was obtained by precipitation in a diethyl ether/acetone solution. No mass reduction occurred in the di-silver (I) sample, indicating that no acetone readily solvates onto the complex. The effects of mechanical grinding and subsequent heating of the di-silver (I) complex were then evaluated.

The results of the PXRD (Fig. S5b) and DSC (Fig. S5c) show that the di-silver (I) complex existed in a composite state consisting of small crystallites and an amorphous domain after mechanical grinding, as observed for the corresponding di-copper (I) complex **1**.

5) Reference

S1 Nishikawa, M., Sano, T., Washimi, M., Takao, K. and Tsubomura, T., *Dalton Trans.*, 2016, **45**, 12127.