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## **Supporting Information**

Fig. S1: PXRD patterns of reaction products of  $CuSO_4 \cdot 5H_2O$  in EG.



Fig. S2: IR spectra of reaction products of  $Cu(NO_3)_2 \cdot 2.5H_2O$  in EG. In accordance with the PXRD results, the COO band indicates the presence of copper(II) oxalate,  $Cu(C_2O_4) \cdot xH_2O$  (x = 0-1).



Fig. S3: DTA-TG diagram of  $Cu(C_2H_4O_2)$  under air. Calculated residual 64.4%.



Fig. S4: Inverse magnetic susceptibility of  $Cu(C_2H_4O_2)$ . The Curie-Weiss fit to the curve above 100 K is shown in red.



Fig. S5: DTA-TG diagram of  $Cu_3(OAc)_2(C_2H_4O_2)_2$  under air. Calculated residual 55.7%.



Fig. S6: Inverse magnetic susceptibility of  $Cu_3(OAc)_2(C_2H_4O_2)_2$ . The Curie-Weiss fit to the curve above 200 K is shown in red.



Fig. S7: PXRD patterns of the reaction products obtained from EG solutions of  $CuCl_2 2H_2O$  or  $CuSO_4 \cdot 5H_2O$  with addition of 2 eq. of NaOAc  $3H_2O$  or 4 eq. of NaOH. Additional washing cycles are necessary to remove  $Na_2SO_4$  which is observed as a byproduct due to its low solubility in EG.



Fig. S8: PXRD patterns of the reaction products of  $Cu(OH)_2$  and  $Cu(OAc)_2 \cdot H_2O$  with DEG (a, b), TrEG (c, d), and TEG (e, f). Black stars in (d, f) mark an unknown phase, corresponding with strong carbonyl bands in the IR spectra (Fig. S14).



Fig. S9: IR spectra of Cu(C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>), the acetate-alkoxide compound (obtained from Cu(OAc)<sub>2</sub>·H<sub>2</sub>O at 120 °C), and liquid DEG.



Fig. S10: DTA-TG diagram of  $Cu(C_4H_8O_3)$  under air. The experimental value is slightly lower than the calculated residual (47.5%).



Fig. S11: SEM images of  $Cu(C_4H_8O_3)$  obtained from  $Cu(OH)_2$  (left) and  $Cu(OAc)_2 \cdot H_2O$  (right).



Fig. S12: IR spectra of  $Cu(C_6H_{12}O_4)$  and liquid TrEG.



Fig. S13: DTA-TG diagram of  $Cu(C_6H_{12}O_4)$  under air. The experimental residual is significantly lower than the calculated one (37.6%). The mass loss observed up to 150 °C is most likely due to water or ethanol molecules still present in the material after drying in vacuum at room temperature.



Fig. S14: IR spectra of products obtained from the reaction of  $Cu(OAc)_2 \cdot H_2O$  with TrEG at 180 °C and TEG at 160 °C. Intense carbonyl bands are visible at ca. 1600 cm<sup>-1</sup>.