

Supporting Information

Halide-mediated electrochemical modification of copper phthalocyanine for humidity sensing applications

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S1 Experimental setup for humidity measurements

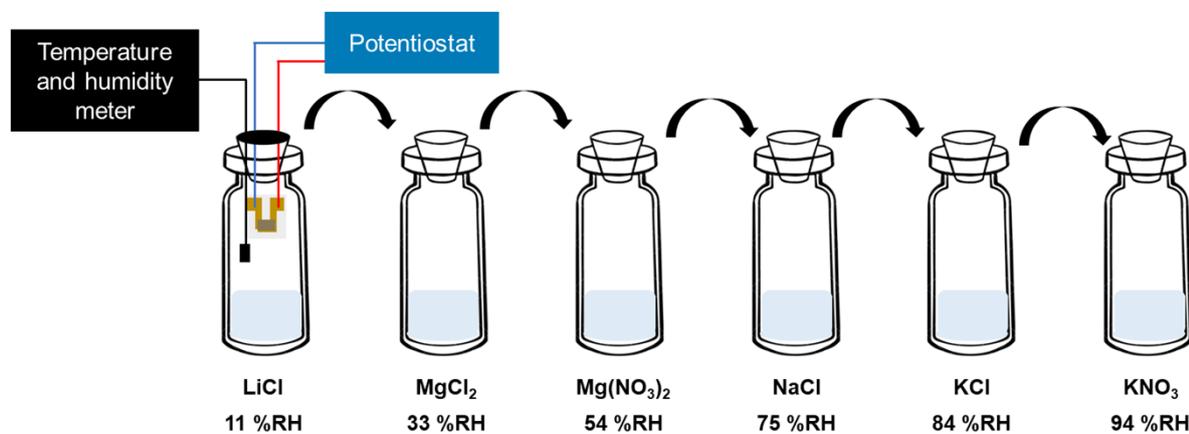


Figure S1: Experimental setup for humidity measurements at various relative humidity (%RH) levels using saturated aqueous salt solutions: LiCl (11 %RH), MgCl₂ (33 %RH), Mg(NO₃)₂ (54 %RH), NaCl (75 %RH), KCl (84 %RH), and KNO₃ (94 %RH).

S2 Effects of exfoliation time: colors of dispersions and powders

Figure S2 displays the dispersions of CuPc after being subjected to exfoliation in 0.50 M LiCl and 1.0 mM PVP at 10 V for durations of 0, 15, 30, 60, and 90 minutes. The image shows a noticeable change in color intensity over time. Initially, at 0 minutes, the CuPc dispersion is vibrant blue. As the exfoliation process progresses, the color subtly darkens and shifts to navy blue/green. The colors of the dry CuPc powder before and after exfoliation are presented in Figure S3.

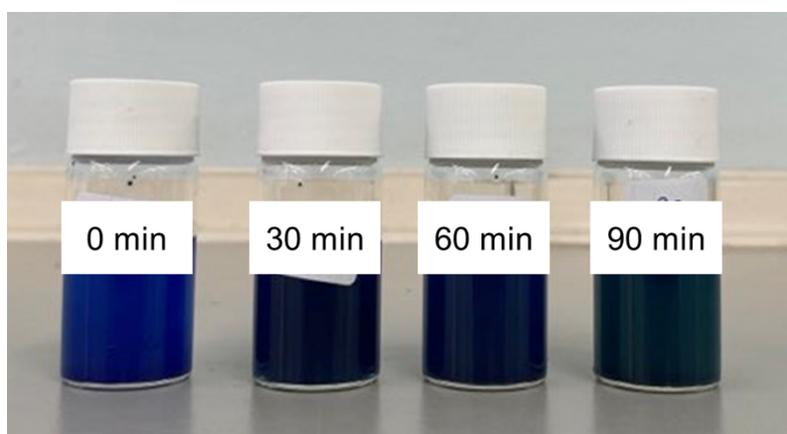


Figure S2: The dispersions of 0.50 mg mL^{-1} CuPc after exfoliation in 0.50 M LiCl and 1.0 mM PVP at 10 V for different durations (0- 90 minutes).

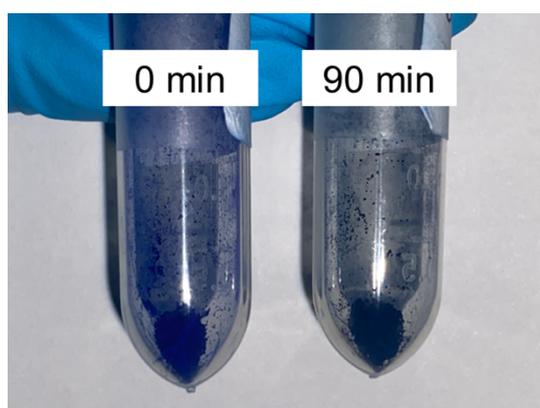


Figure S3: CuPc powder before exfoliation (**left**) and after exfoliation (**right**) in 0.50 M LiCl and 1.0 mM PVP at 10 V for 90 minutes.

S3 Effects of electrolyte cations and anions

Figure S4 demonstrates that the exfoliation of CuPc in Na_2SO_4 and Li_2SO_4 results in no color changes in the suspension. Conversely, the exfoliation of CuPc in NaCl and LiCl leads to a color change in the dispersions, with both resulting in the same new color.

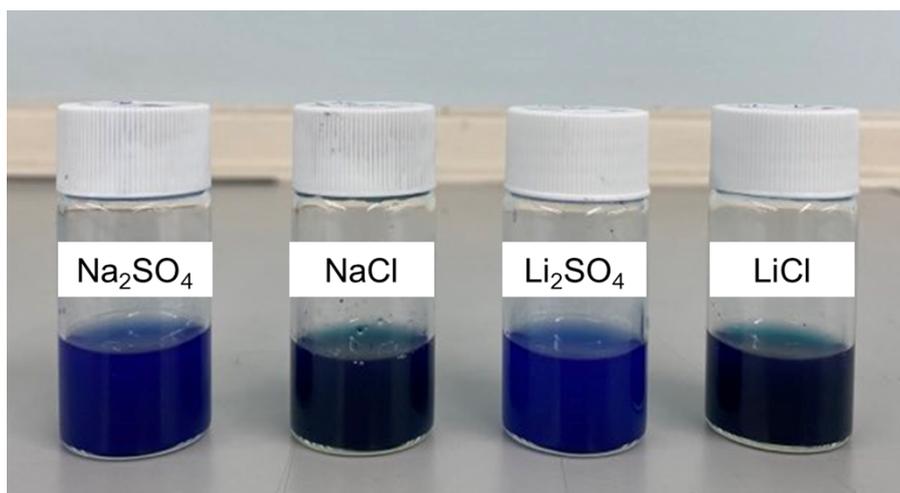


Figure S4: The dispersions of 0.50 mg mL^{-1} CuPc after exfoliation in 0.50 M Na_2SO_4 or NaCl or Li_2SO_4 or LiCl in the presence of 1.0 mM PVP at 10 V for 60 minutes.

The unchanged color of the dispersion from the exfoliation of CuPc in Na₂SO₄ corresponds to the stable UV-vis spectra shown in Figure S5. Meanwhile, the UV-vis spectra for the exfoliation in chloride electrolytes are detailed in the main text.

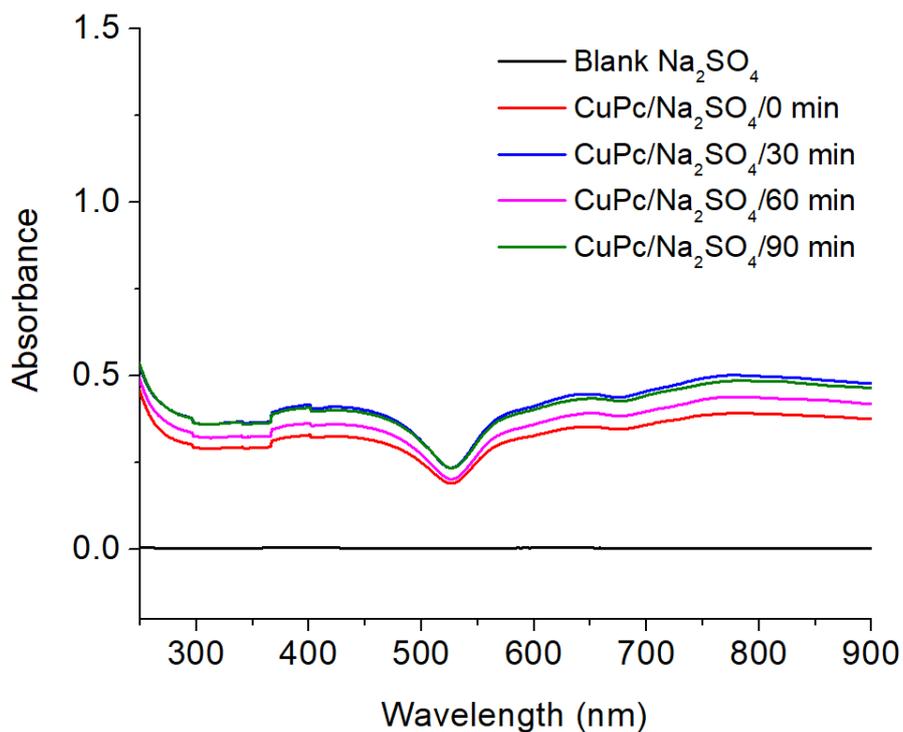


Figure S5: UV-vis spectra of 0.5 mg mL⁻¹ CuPc after exfoliation in 0.50 M Na₂SO₄ and 1.0 mM PVP at 10 V for 0, 30, 60 and 90 minutes.

When changing the electrolyte in the exfoliation process to LiBr, the resulting suspension shifted from blue to green, similarly to the effect observed with LiCl. However, the suspension appeared even greener with LiBr than with LiCl, as depicted in Figure S6. This shift vividly demonstrates the interaction between halides and CuPc during the bipolar electrochemical exfoliation process. The structures of the resulting materials are analyzed using XPS, as detailed in the main text and Section S4.

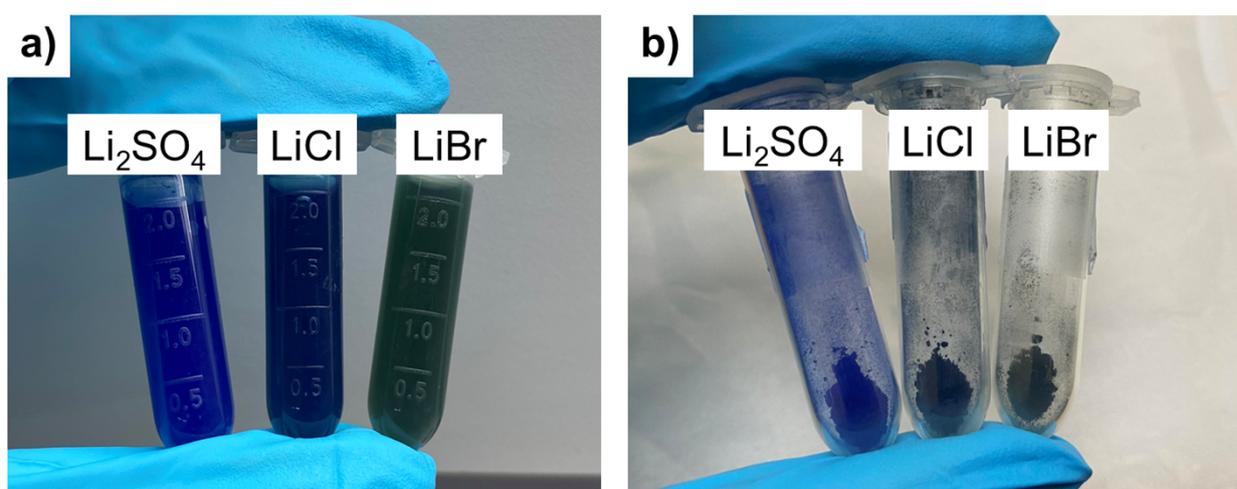


Figure S6: a) The dispersions and b) the dried powder of CuPc after exfoliation in 0.50 M Li₂SO₄ or LiCl or LiBr in the presence of 1.0 mM PVP at 10 V for 90 minutes.

S4 XPS spectra of CuPc before and after exfoliation

Figure S7 presents the X-ray photoelectron spectroscopy (XPS) spectra of copper phthalocyanine (CuPc) before exfoliation. The Cu 2p spectrum features two primary peaks corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2} spin-orbit components at approximately 933 eV and 953 eV, respectively, accompanied by satellite peaks indicative of copper in the Cu(II) oxidation state. The C 1s region reveals a diverse set of peaks: C–H and C–C bonds around 284.8 eV, C=O functionalities near 287 eV, and O–C=O groups at about 289 eV, alongside a π – π^* satellite peak, highlighting aromatic or conjugated systems. In the O 1s spectrum, distinct peaks at 532 eV for C–O bonds, 531 eV for C=O groups, and 530 eV potentially for metal-oxygen bonds or more oxidized carbon species. Lastly, the N 1s spectrum features peaks at 399 eV and 401 eV, associated with C=N–C linkages and nitrogen bonded to carbonyl groups, respectively.

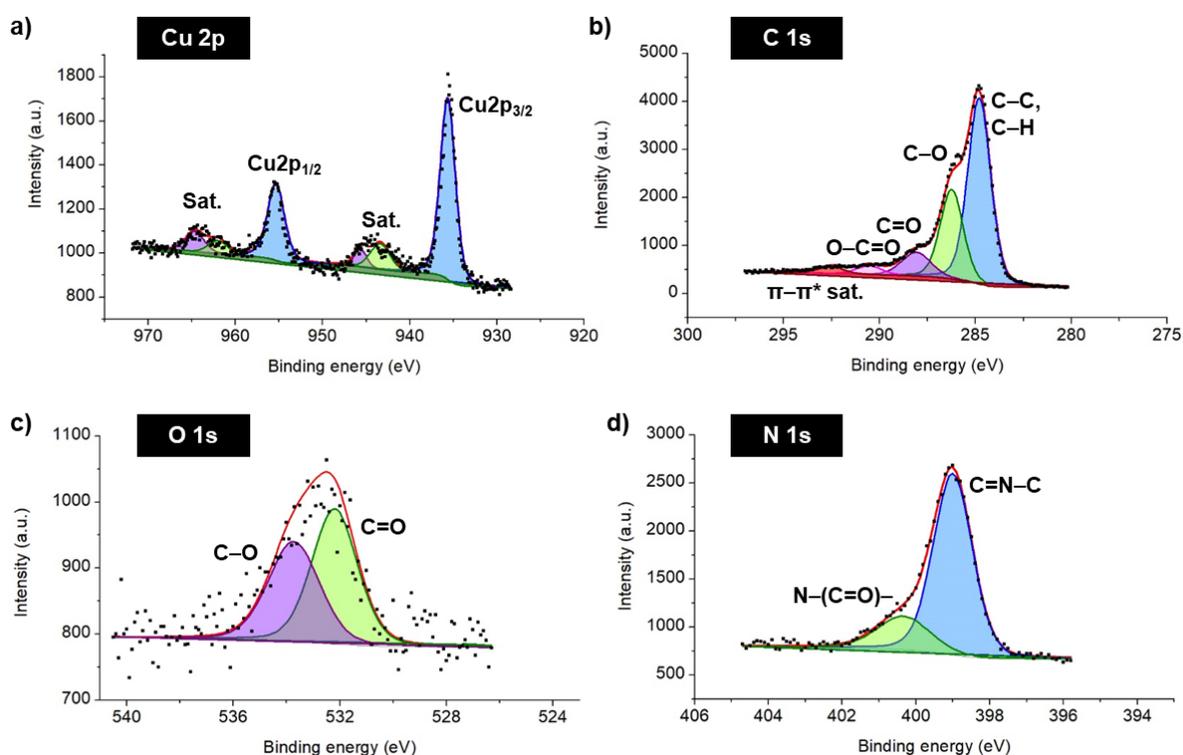


Figure S7: XPS spectra of CuPc before exfoliation, showing peaks for **a) Cu 2p, b) C 1s, c) O 1s, and d) N 1s.**

Figure S8 illustrates the X-ray photoelectron spectroscopy (XPS) spectra of copper phthalocyanine (CuPc) after exfoliation in 0.50 M LiCl at 10 V for 90 minutes, capturing significant changes in the electronic states and chemical interactions of copper, chlorine, carbon, oxygen, and nitrogen. The Cu 2p spectrum exhibits two principal peaks associated with Cu 2p_{3/2} and Cu 2p_{1/2} at approximately 933 eV and 953 eV, respectively. Additionally, satellite peaks and Cu–Cl peaks are present, indicative of copper-chloride interactions. This suggests the incorporation of chlorine into the copper sites during exfoliation. The Cl 2p region shows two pairs of distinct peaks, corresponding to Cl 2p_{3/2} and Cl 2p_{1/2}. One pair is likely associated with the formation of Cu–Cl bonds, while the other pair may be attributed to the formation of C–Cl bonds. In the C 1s spectrum, the presence of multiple carbon bonding environments is evident, with peaks indicative of C–H and C–C at around 285 eV, C–O and C–Cl bonds at around 286 eV, C=O groups at 287 eV, and O–C=O structures around 289 eV, along with a π - π^* satellite peak that highlights the aromatic integrity of the CuPc. The O 1s spectrum features a prominent peak for C=O at approximately 531 eV and a broader peak for C–O bonds. Lastly, the N 1s spectrum displays peaks for C=N–C linkages typical of phthalocyanine structures at around 399 eV and for nitrogen associated with carbonyl groups at about 401 eV.

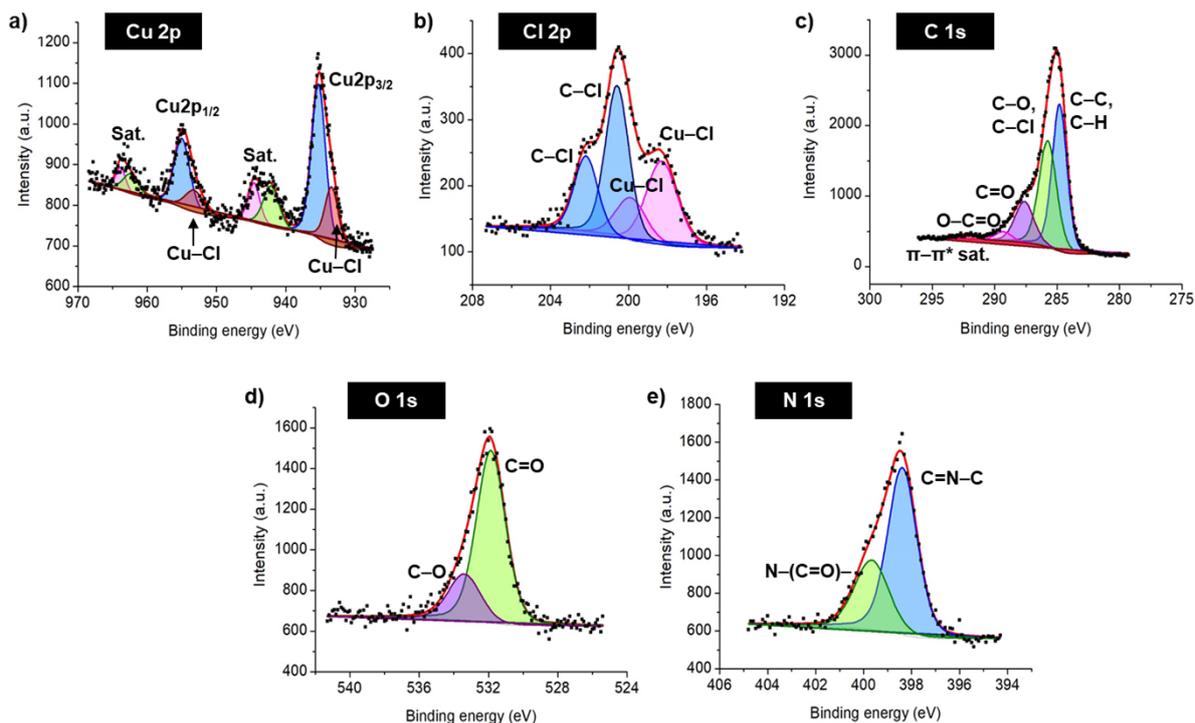


Figure S8: XPS spectra of CuPc after exfoliation in 0.50 M LiCl at 10 V for 90 minutes, showing peaks for **a) Cu 2p**, **b) Cl 2p**, **c) C 1s**, **d) O 1s**, and **e) N 1s**.

Figure S9 displays the X-ray photoelectron spectroscopy (XPS) spectra of copper phthalocyanine (CuPc) after undergoing exfoliation in 0.50 M LiBr at 10 V for 90 minutes. The Cu 2p spectrum features prominent peaks at approximately 933 eV and 953 eV for Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, accompanied by satellite peaks and specific peaks indicating copper-bromide (Cu-Br) interactions, suggesting the formation of copper-bromide bonds during the exfoliation process. The Br 3d spectrum shows distinct peaks for Br 3d_{5/2} and Br 3d_{3/2}, with shifts that imply variations in bromine chemical environments, possibly due to Cu-Br and C-Br bonding. In the C 1s spectrum, multiple carbon bonding environments are evident, with peaks at 285 eV for C-H and C-C bonds, 287 eV for C-O and C-Br groups, and 289 eV for O-C=O structures, alongside a π - π^* satellite peak that highlights the preserved aromatic

structure of CuPc. The O 1s spectrum features a strong peak for C=O at 531 eV and a broader peak for C–O bonds. Lastly, the N 1s spectrum shows peaks at 399 eV for C=N–C linkages and at 401 eV for nitrogen associated with carbonyl groups.

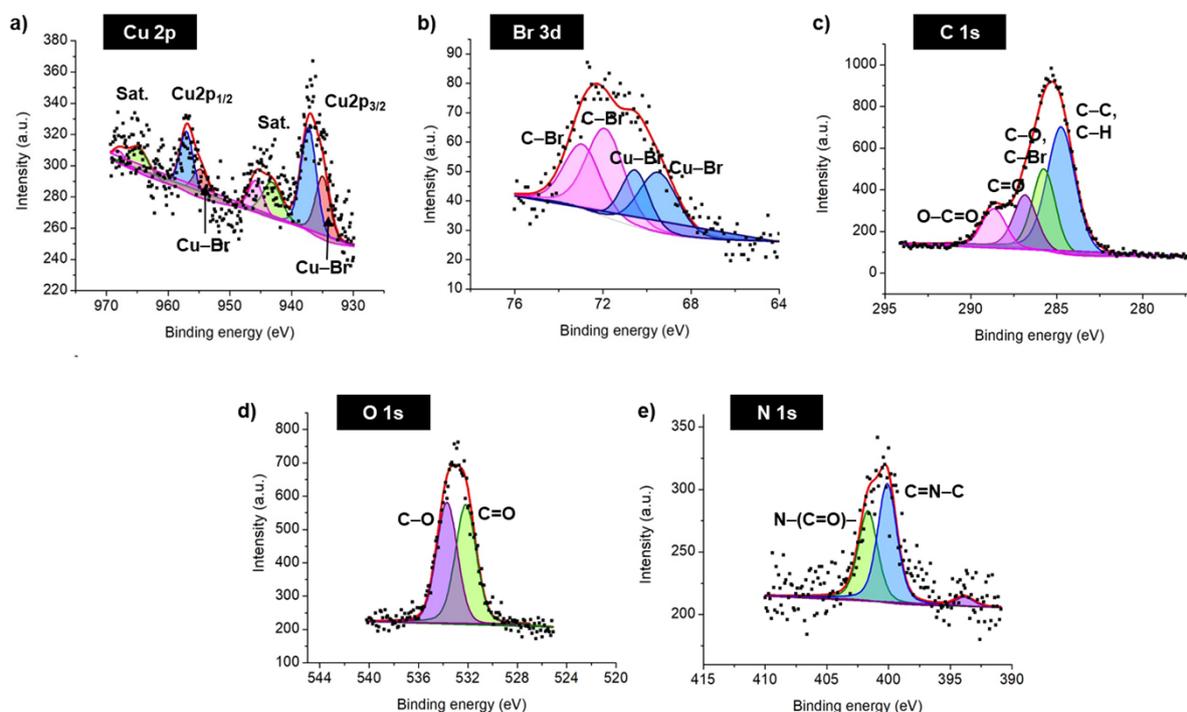


Figure S9: XPS spectra of CuPc after exfoliation in 0.50 M LiBr at 10 V for 90 minutes, showing peaks for **a)** Cu 2p, **b)** Br 3d, **c)** C 1s, **d)** O 1s, and **e)** N 1s.

Figure S10 presents the X-ray photoelectron spectroscopy (XPS) spectra of polyvinylpyrrolidone (PVP) powder. In the C 1s spectrum, there are distinct peaks representing various carbon bonding environments: a peak at approximately 285 eV for C–C and C–H bonds, indicative of the backbone of the polymer; a peak around 286 eV for C–O bonds; and another peak at about 289 eV for C=O functionalities. The O 1s spectrum features two major peaks: one at 531 eV for C=O groups and another broader peak at 533 eV for C–O bonds. The N 1s spectrum displays two significant peaks: one at 399 eV for C=N–C linkages, which are

characteristic of the pyrrolidone ring in PVP, and another at 401 eV for N-(C=O)-, indicating nitrogen atoms linked to carbonyl groups.

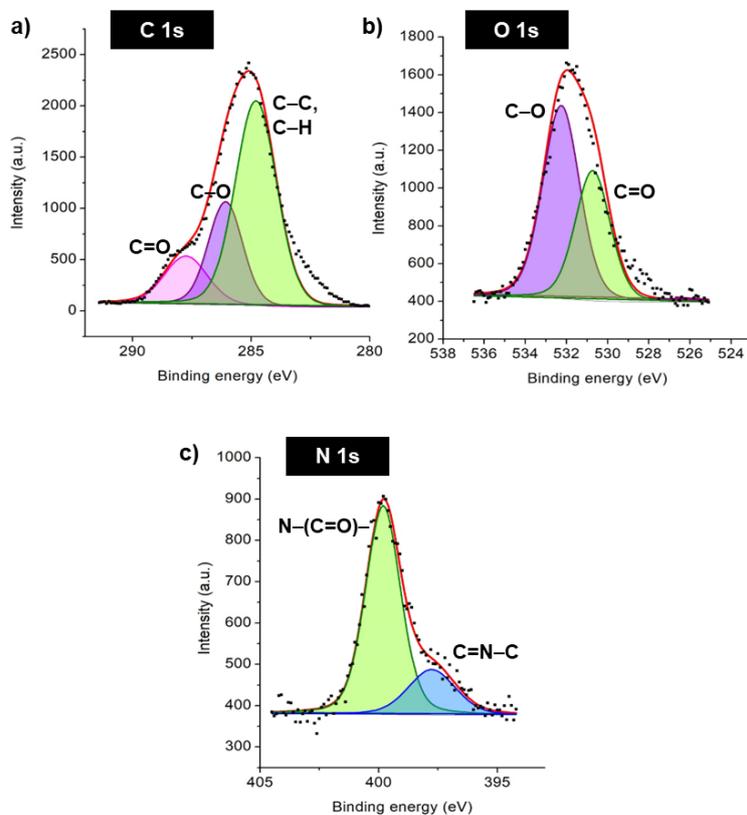


Figure S10: XPS spectra of PVP powder, showing peaks for a) C 1s, b) O 1s, and c) N 1s.

S5 Current-voltage characteristics of the unmodified CuPc/PVP

Figure S11 demonstrates the current-voltage characteristics of the unmodified CuPc/PVP under varying humidity levels, ranging from 11 to 94 %RH. The relative humidity response (S), calculated according to equation 1 (main text), is shown in the inset of Figure S11, with the maximum response of $4.7 \times 10^3\%$.

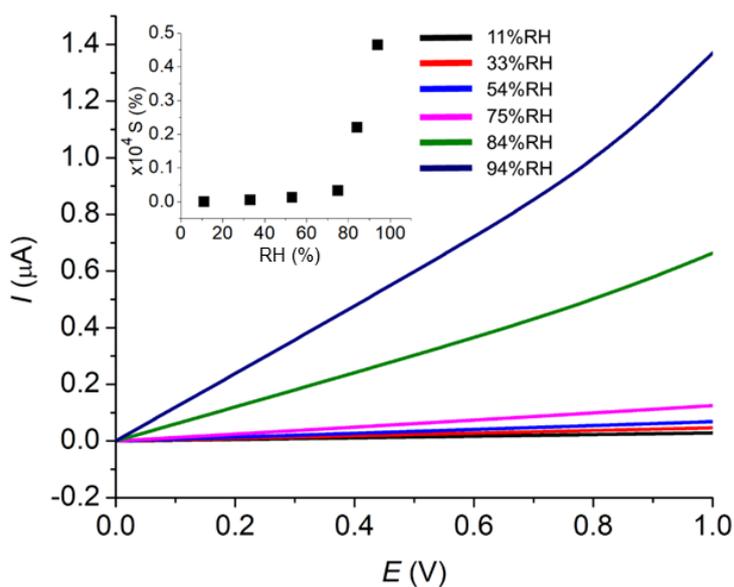


Figure S11: Current-voltage characteristics of the unmodified CuPc/PVP sensor across varying relative humidity (%RH) levels. The inset shows the plot of the humidity response (S) as a function of %RH.

S6 Schematic illustration of the proposed detection mechanism

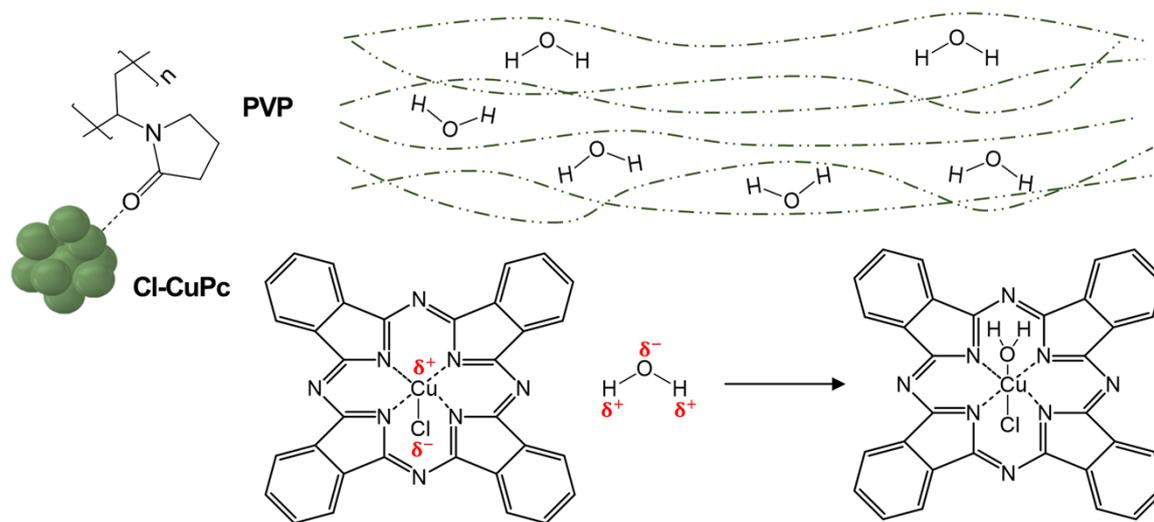


Figure S12: Schematic illustration of the proposed detection mechanism of the Cl-CuPc/PVP humidity sensor