

Supporting Information

A Novel n-Type Organosilane – Metal Ion Hybrid of Rhodamine-B and Copper Cation for Low Temperature Thermoelectric Materials

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Table S1. Difference in geometry optimization calculation energies, relative to the optimum, of RBS with Cu²⁺ in various positions. Position 6 proved to be the optimum by 0.87 eV. The Cu²⁺ location for this minima is located between the O and N of RBS, exhibiting Schiff-base behavior of the Cu-RBS complex.

Position	ΔE (eV)
1	0.87
2	1.40
3	1.60
4	2.13
5	2.80
6	0
7	1.20

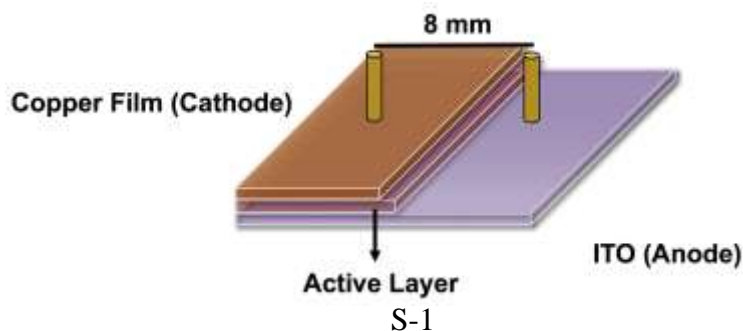


Figure S1: A schematic diagram of the device structure used to conduct electric and thermoelectric property measurements.

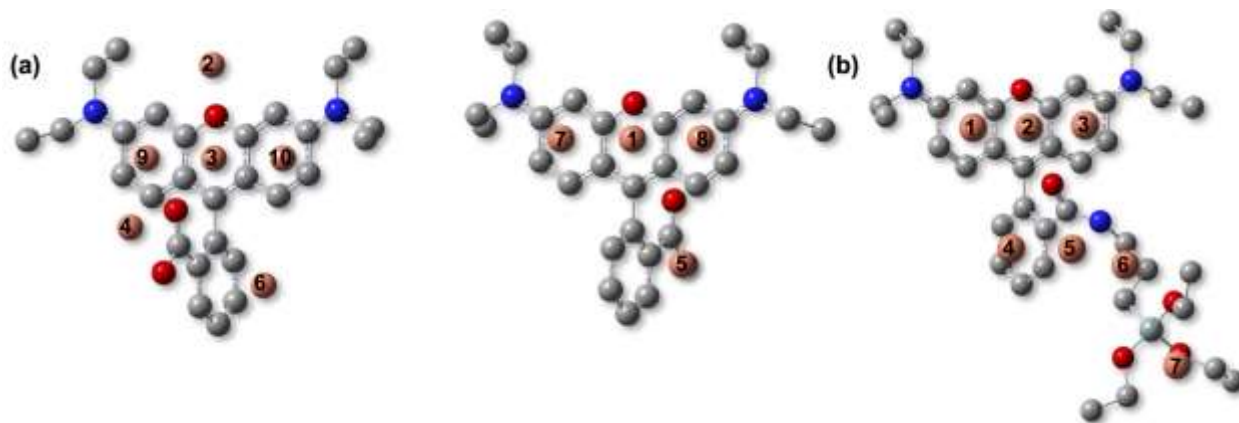


Figure S2: Optimized geometries of RB (a) and RBS (b) with the Cu atom in various locations used to elucidate the minimum energy, and therefore most likely, position of Cu^{2+} relative to each molecular structure. The optimum for RB was found to be position 9, with Cu^{2+} isolated to the xanthene ring structure on the same side as the benzoic acid portion of RB. Position 6 was found to be the minimum for RBS, with Cu^{2+} located next to the N and O of the silane tail.

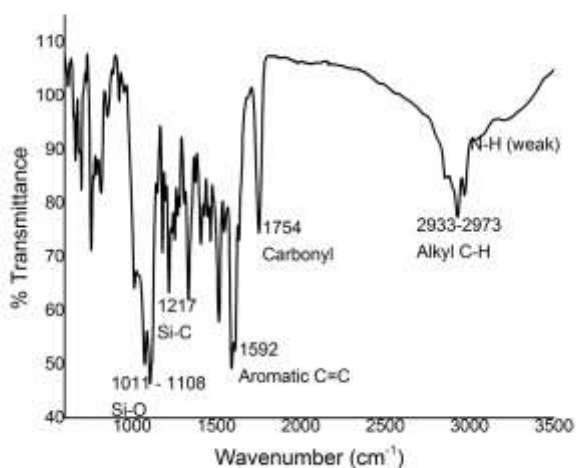


Figure S3: FT-IR spectrum of Rhodamine-B silane.

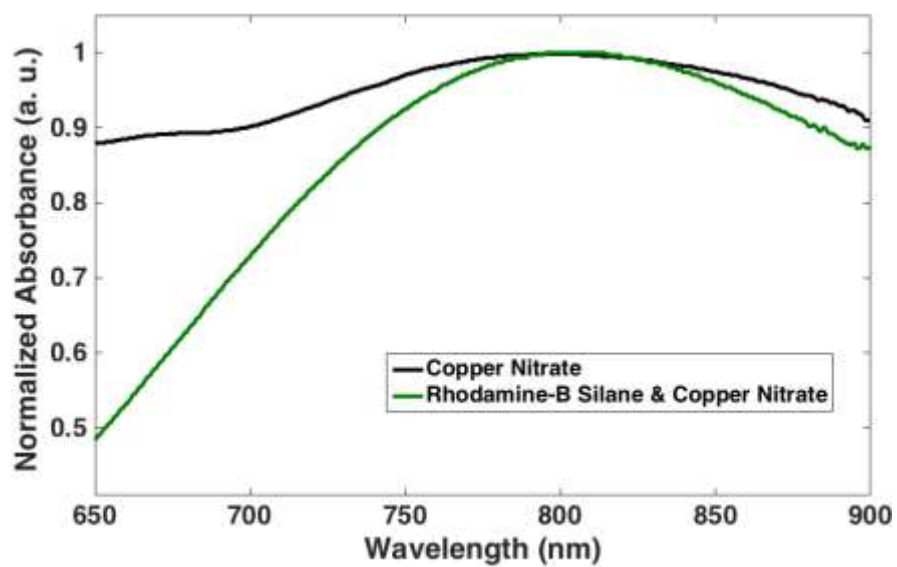


Figure S4: UV-visible spectra for Cu^{+2} and Cu-RBS complex in water exhibiting a slight blue-shift in absorbance. This observation provides further evidence that Cu^{2+} forms a Schiff-base complex with RBS. π -electron donation from Cu^{2+} onto RBS stabilizes the metal d-orbitals, resulting in an increase in the energy barrier between the t_{2g} and e_g d-d electronic transition.

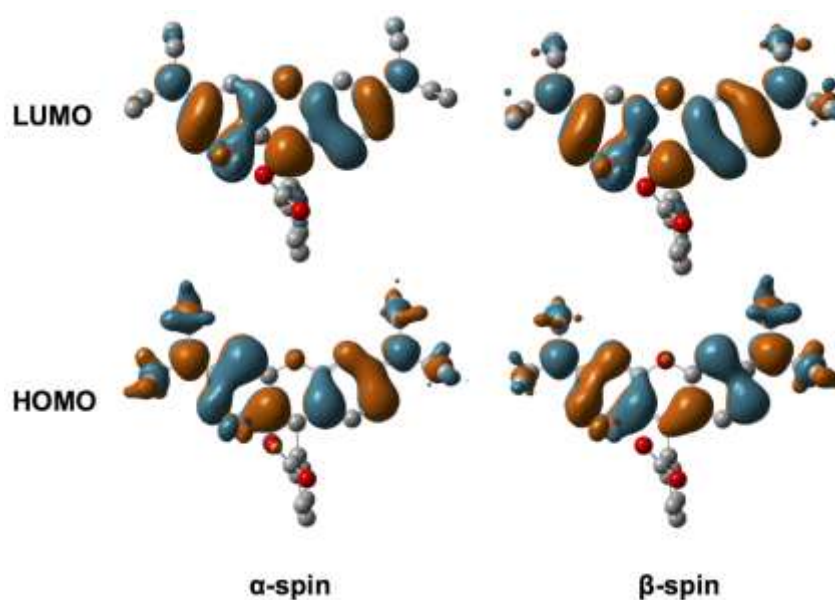
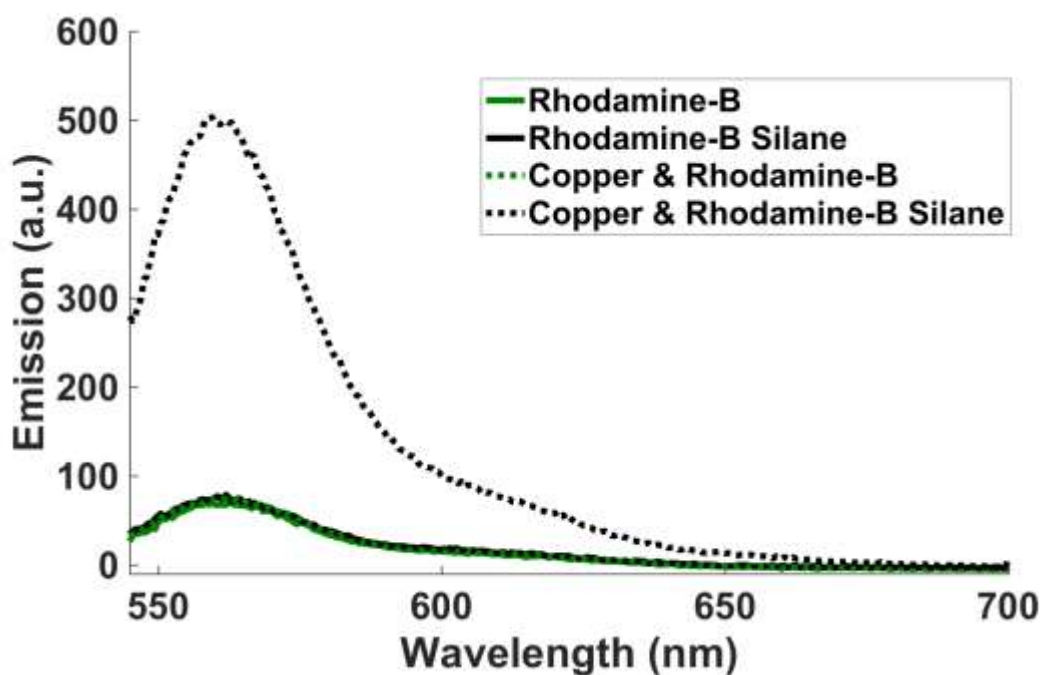


Figure S5: Alpha- and beta-spin molecular orbital contours of the lowest energy transition for Cu-RB elucidated by B3LYP method 6-31G basis set while using LANL2DZ for Cu^{2+} only. The



contours indicate that a metal-to-ligand charge transfer is unique to Cu-RBS.

Figure S6: Fluorescence emission spectra of RB, RBS, Cu-RB, and Cu-RBS displaying the large increase in emission upon complexation of Cu^{2+} to RBS, which is not observed for any other species.

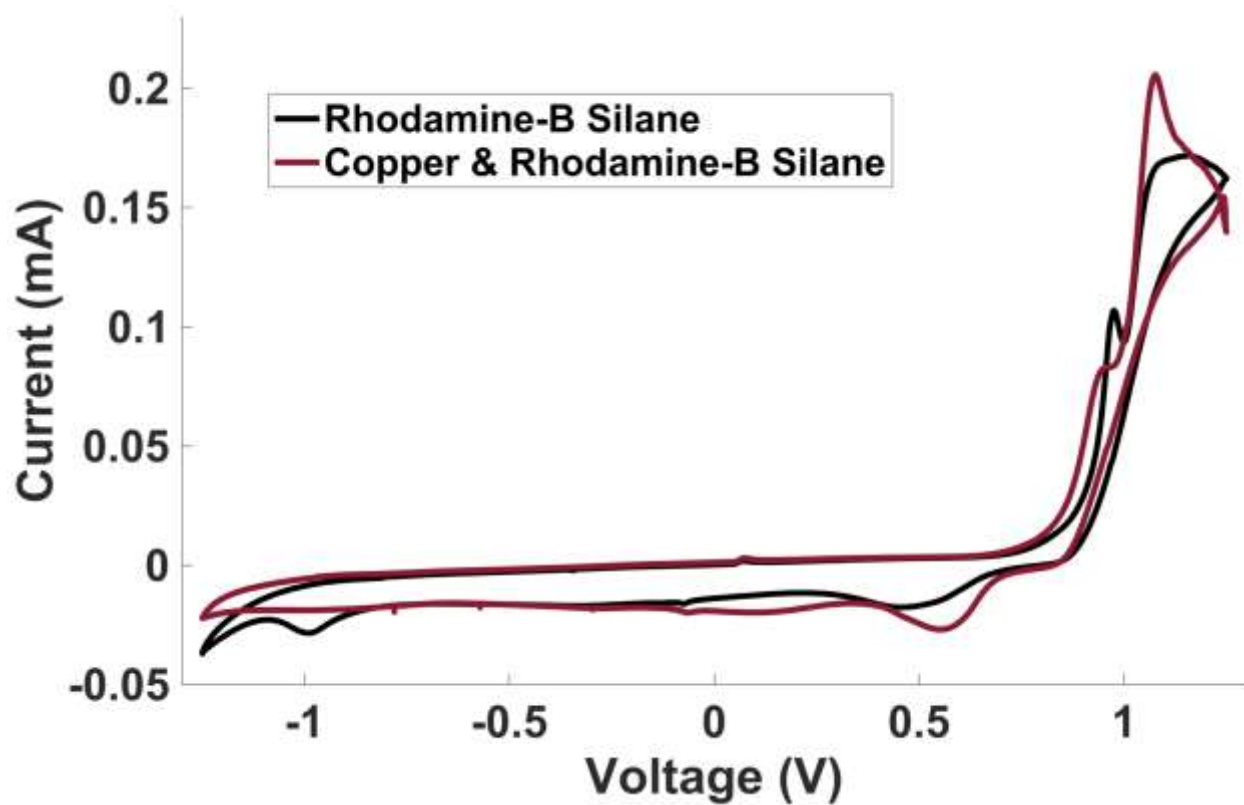


Figure S7: Cyclic voltammetry graphs for RBS and Cu-RBS.

