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Insights on spin delocalization and spin polarization mechanisms in crystals of azido Cu (II) dinuclear complexes through the Electron Spin Density Source Function

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S1. Source Function reconstructed partial densities (End-On complex)

Source Function (SF) reconstructed partial spin densities, $S_s(\Omega_{subset})(\mathbf{r})$ and their magnetic, $S_{s,mag}(\Omega_{subset})(\mathbf{r})$, and relaxation, $S_{s,relax}(\Omega_{subset})(\mathbf{r})$, components are reported in Figures S1-S2 for the End-On (EO) ferromagnetic (FM) complex at both the CASSCF(6,6) and UB3LYP levels.

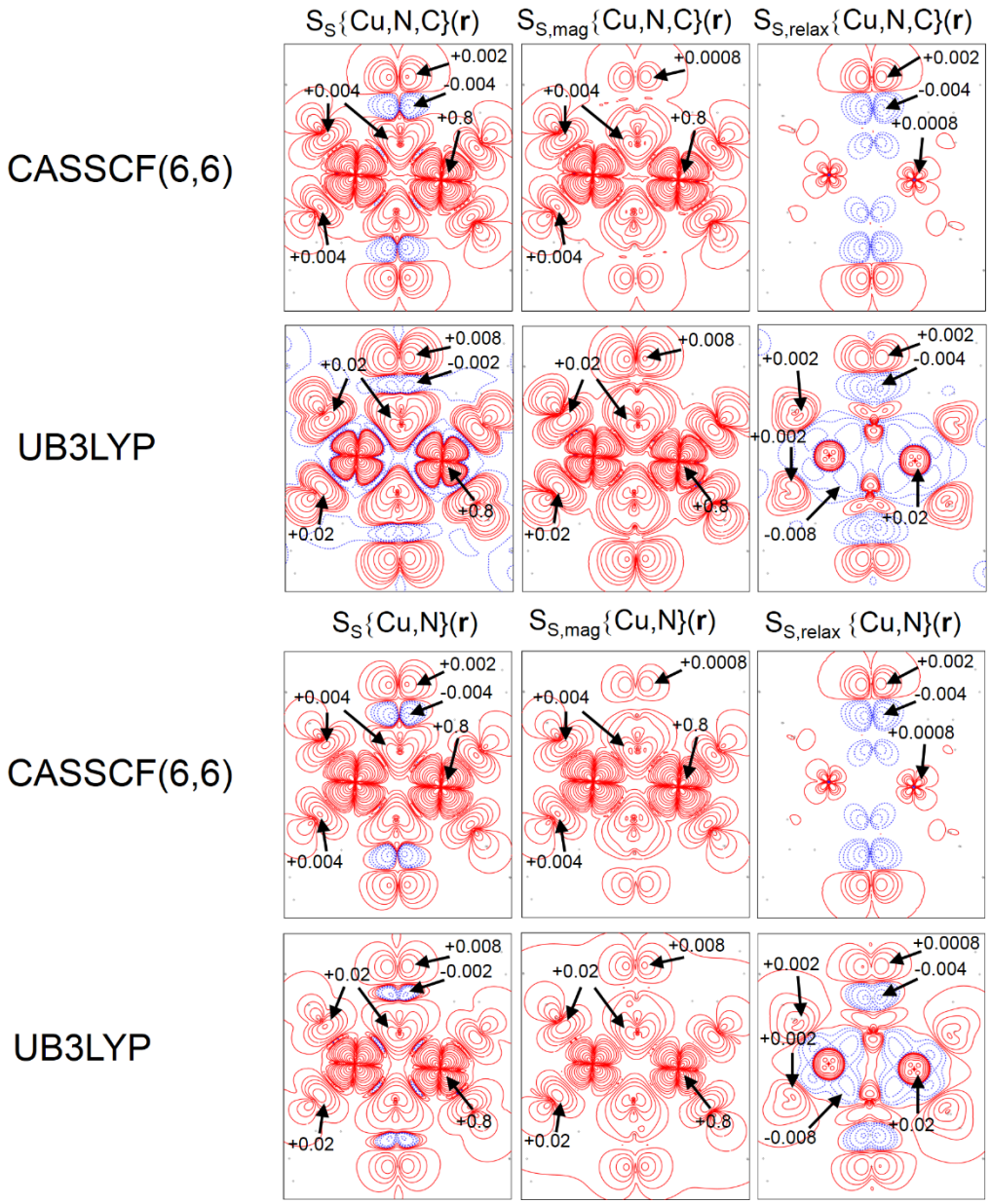

Figure S1 End-On FM complex: CASSCF(6,6) and UB3LYP contour plots of the partially SF reconstructed spin densities, $S_s(\Omega_{subset})(\mathbf{r})$, and of its magnetic, $S_{s,mag}(\Omega_{subset})(\mathbf{r})$, and relaxation, $S_{s,relax}(\Omega_{subset})(\mathbf{r})$, components in the least squares plane of the four N ligand atoms around each Cu. In the maps, {Cu, N, C} denotes the subset of system's atoms including the two Cu atoms, all N atoms and the C atoms of the pyridine rings, while {Cu, N} denotes the subset obtained by excluding the C atoms from the former. Isocontours: red positive and, dotted blue, negative contour values; contour maps are drawn at interval of $\pm(2,4,8)\cdot 10^n$, $-4 \le n \le 0$ atomic units (au)).

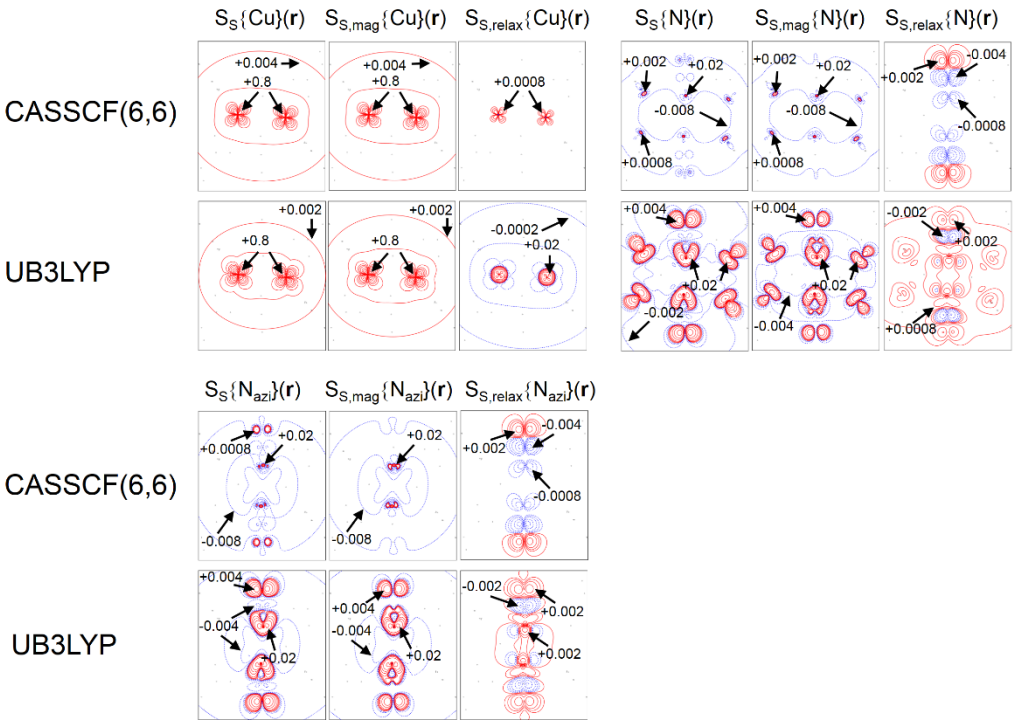

Figure S2 End-On FM complex: CASSCF(6,6) and UB3LYP contour plots of the partially SF reconstructed spin densities, $S_s(\Omega_{subset})(\mathbf{r})$, and of its magnetic, $S_{s,mag}(\Omega_{subset})(\mathbf{r})$, and relaxation, $S_{s,relax}(\Omega_{subset})(\mathbf{r})$, components in the least squares plane of the four N ligand atoms around each Cu. In the maps, {Cu}, {N} and $\{N_{azi}\}$ denote the subsets of system's atoms including the two Cu atoms, all N atoms and only the N atoms of the azido groups, respectively. Same colour codes and isovalue contours as in Figure S1.

S2. Source Function percentage contributions (End-On Complex)

SF percentage contributions to the electron spin density s, along with their magnetic and relaxation components, are reported at selected reference points, *rps,* for the End-On (EO) (Figure S3) complex at both the UB3LYP and CASSCF(6,6) levels.

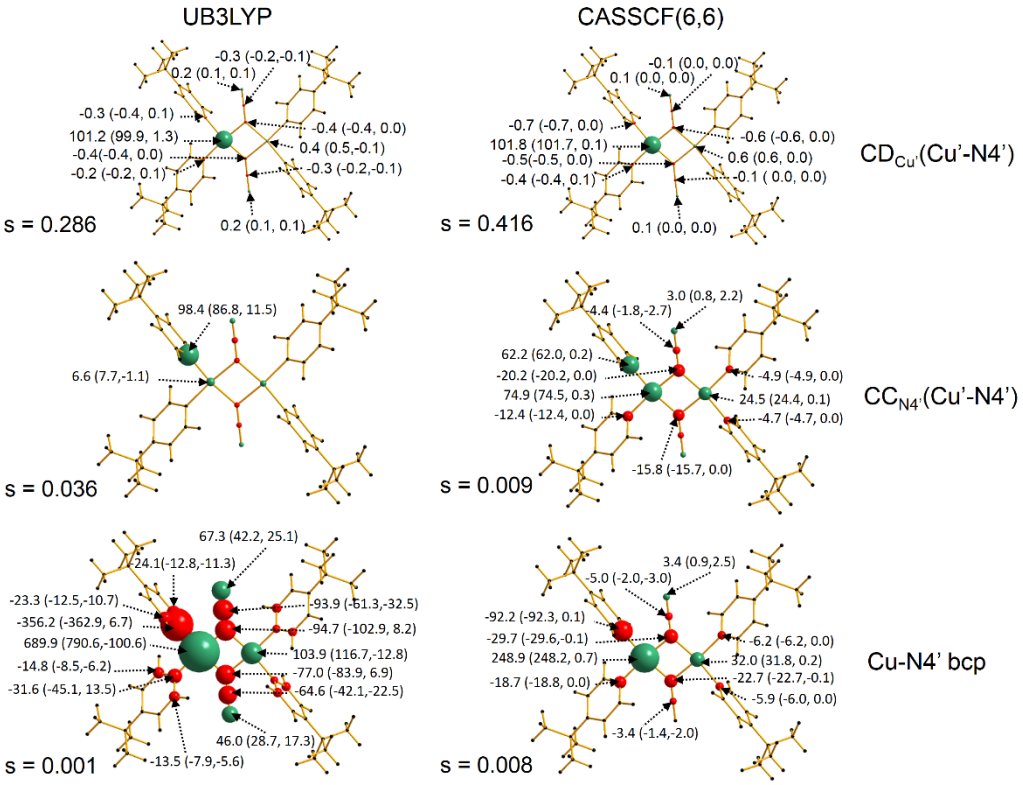

Figure S3 End-On FM complex: UB3LYP and CASSCF(6,6) SF percentage contributions to the electron spin density s (magnetic and relaxation components in parentheses) at selected reference points, *rps* (Table 2 of the manuscript). Rps: CD$_{Cu'}$(Cu'-N4') denotes the Charge Depletion in the Valence Shell Charge Depletion (VSCD) of the Cu atom and lying along Cu'-N4', while CC$_{N4'}$(Cu'-N4') denotes the Charge Concentration in the Valence Shell Charge Concentration (VSCC) of the N4' atom and lying almost along Cu'-N4'. The s values at *rps* are in au. Green (red) atomic balls denote an α (β) effect on the density at the reference point. SF percentage contributions are positive or negative whether they concur or oppose to reconstruct the corresponding density value at the *rp*.

S3. Comparison of spin resolved components *vs* spin densities (End-End Complex)

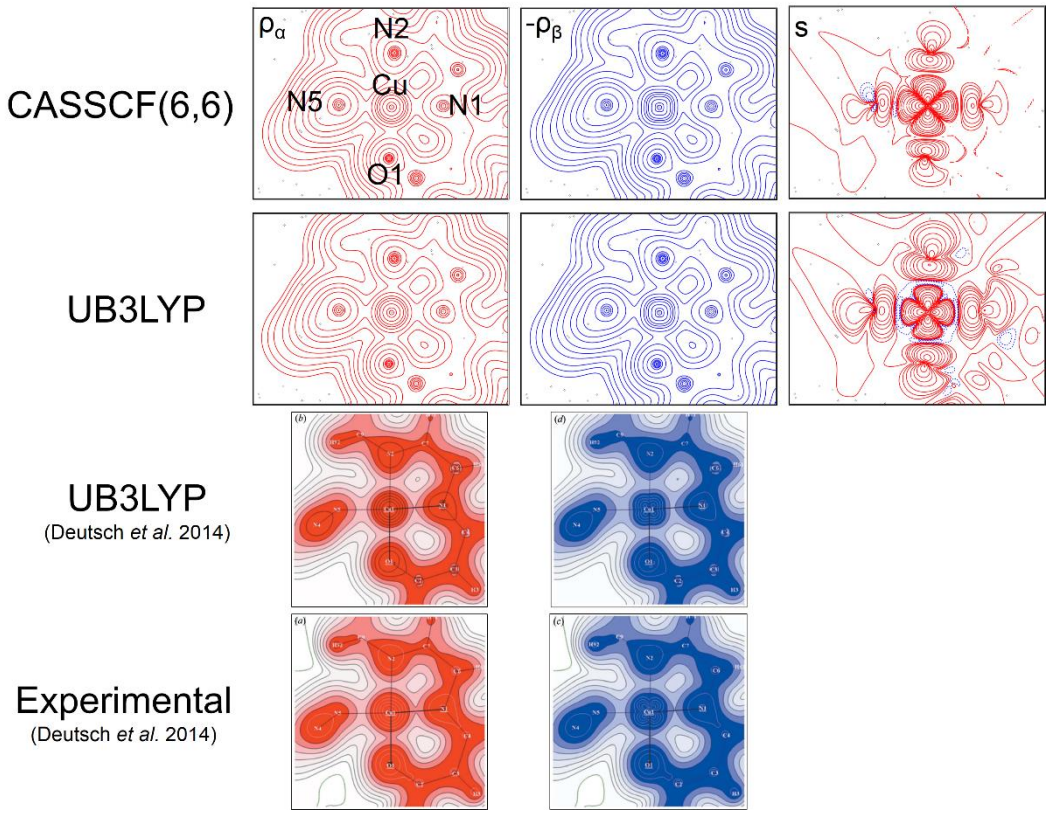

Figure S4 End-End (EE) FM complex: CASSCF(6,6) and UB3LYP (first and second row respectively) contour plots of spin resolved, ρ_α, $-\rho_\beta$ electron densities and of electron spin density s= $\rho_\alpha - \rho_\beta$, in the least square planes of the Cu-O and of the three shorter Cu-N bonds. Same colour codes and isovalue contours as in Figure 1 main text. The calculated and the experimental ρ_α and $-\rho_\beta$ obtained by Deutsch et al. are showed in the third and fourth rows as a comparison. Contours are drawn at values $0.01 \cdot 2^n$ e Å^{-3}, n=0-12 (adapted from Deutsch et al., 2014, reproduced with permission of the International Union of Crystallography).