Supplementary Figures and Tables

Figure S1: Computed logarithmic fractional abundances for the Cu-ligand systems for three different ligands, based on published data[1-3]: (a) Br^- (*1*), (b) Cl^- (*2*), and (c) NO_2^- (*3*). The concentration dependence of the fractional abundance of each Cu-ligand complex species at equilibrium for an analytical Cu^{2+} concentration of 0.01 M is calcuated from the reported stability constants, based on the procedure outlined in Ref. [4]

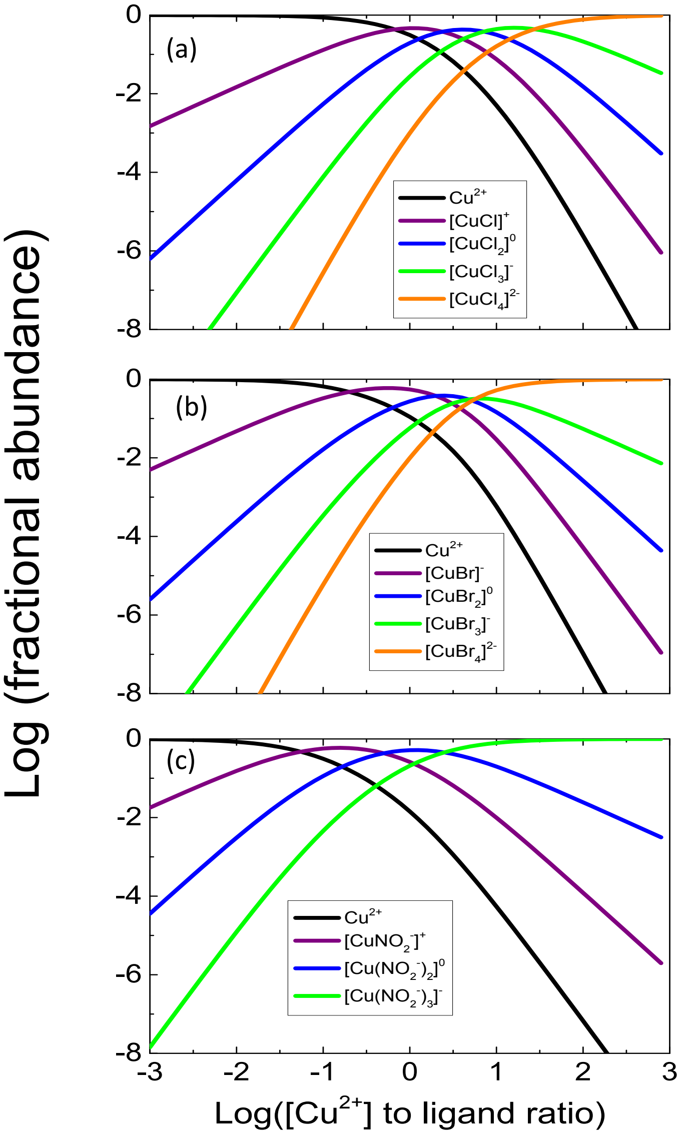

Figure S2: Peak position as a function of ligand substitution level *x*, calculated within the A) CI, B) WC, C) GD, and D) EA schemes described in the main text. The *x* values for the EA scheme are determined by weighting the fractional abundances in Figure S1 at each tested concentration (L^-:Cu^{2+} ratios = 1:1, 10:1, 100:1, 500:1).

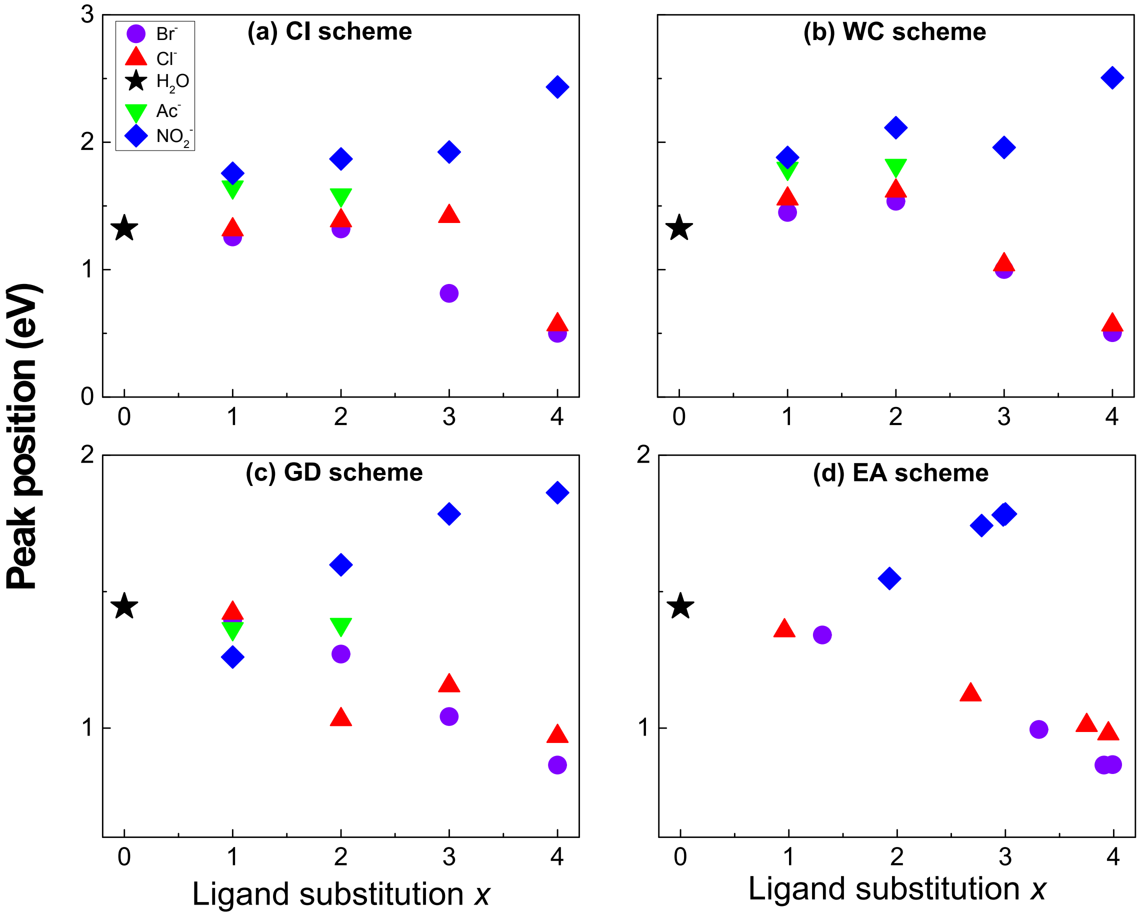

Figure S3: Oscillator strength as a function of ligand substitution level *x*, calculated within the (a) CI, (b) WC, (c) GD, and (d) EA schemes described in the main text. The *x* values for the EA scheme are determined by weighting the fractional abundances in Figure S1 at each tested concentration (L^-:Cu^{2+} ratios = 1:1, 10:1, 100:1, 500:1).

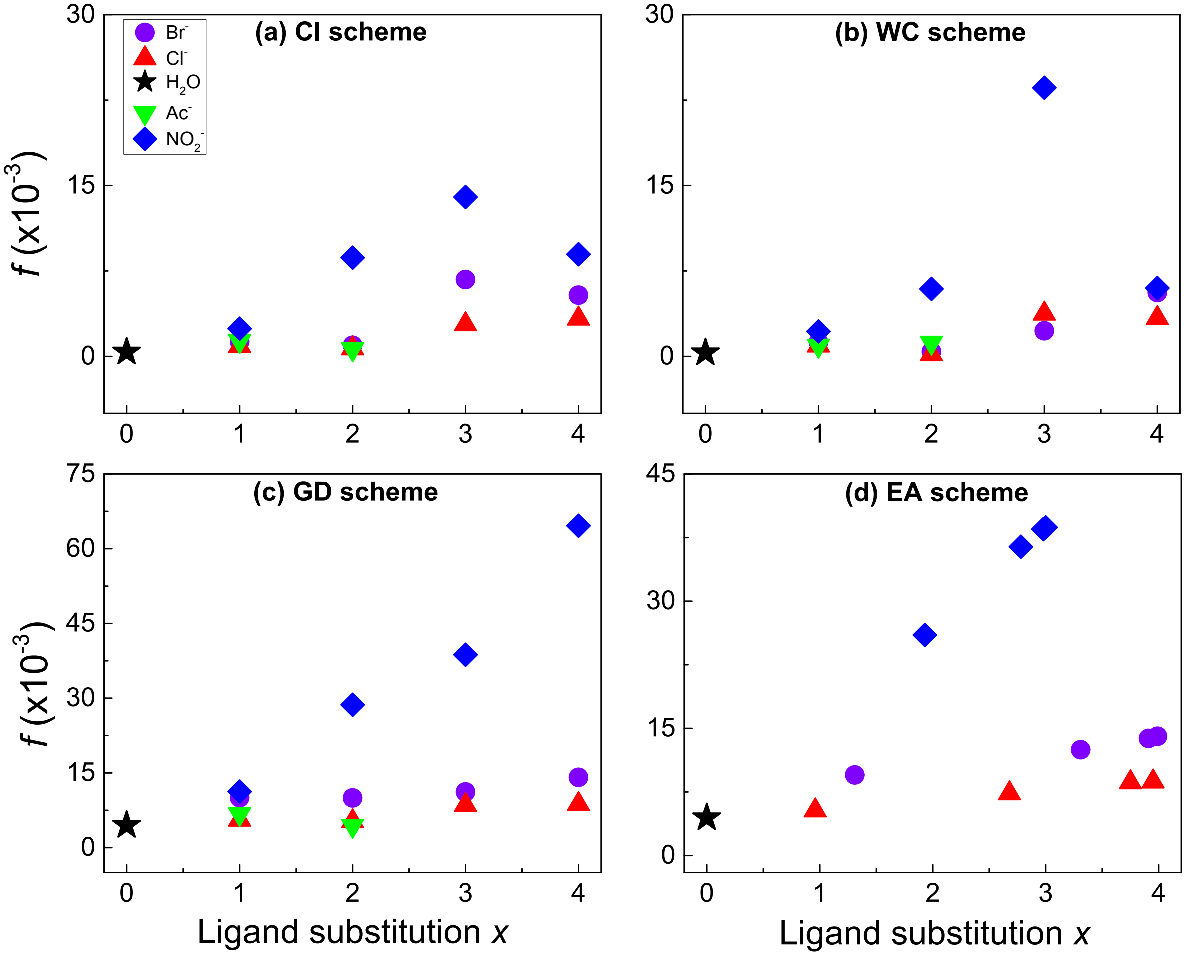

Figure S4: Optical absorption spectra of 0.01 M Cu^{2+} aqua solution collected at two different temperatures; (a) 25 °C and (b) 60 °C.

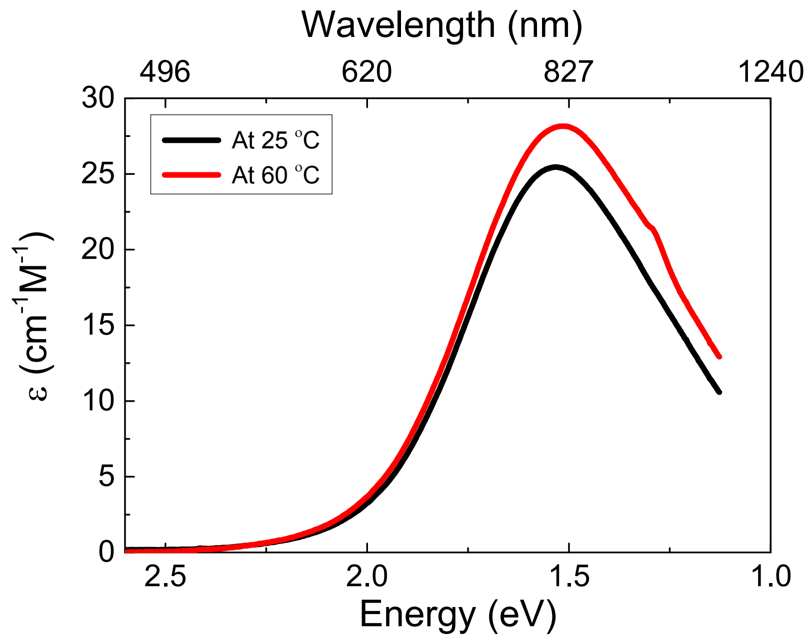

Figure S5: Computed peak profile for the Cu^{2+} aqua complex decomposed into the four contributing transitions Δ_i, including electronic and thermal/solvent broadening effects.

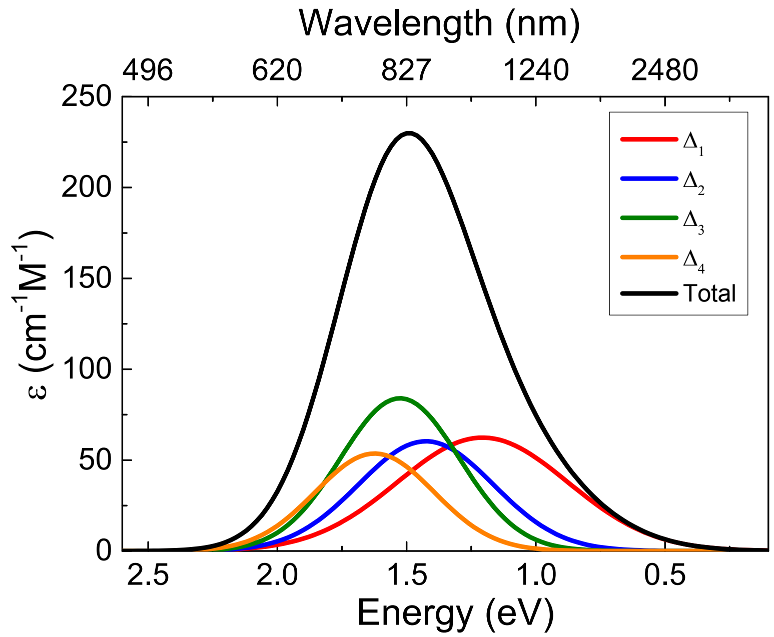

Table S1: Relative fractions p_n of first-shell coordinations n for Cu^{2+} at different levels of ligand substitution x, based on FPMD simulations.

Substituted ligand	**Level of substitution (*x*)**	**Fraction of n = 3**	**Fraction of n = 4**	**Fraction of n = 5**	**Fraction of n = 6**	**Average coordination number**
None (H_2O)	0	0	0.155	0.806	0.038	**4.88**
Br^-	1	0.001	0.437	0.55	0.012	**4.57**
	2	0.002	0.563	0.431	0.005	**4.44**
	3	0.097	0.84	0.062	0.002	**3.97**
	4	0.012	0.96	0.028	0	**4.02**
Cl^-	1	0.001	0.525	0.459	0.014	**4.49**
	2	0.013	0.733	0.222	0.03	**4.27**
	3	0.043	0.845	0.102	0.01	**4.08**
	4	0.001	0.908	0.088	0.004	**4.10**
Ac^-	1	0	0.464	0.524	0.011	**4.55**
	2	0.109	0.622	0.261	0.008	**4.17**
NO_2^-	1	0.017	0.724	0.237	0.022	**4.26**
	2	0	0.599	0.389	0.012	**4.41**
	3	0.004	0.486	0.491	0.019	**4.53**
	4	0	0.448	0.525	0.026	**4.58**

Table S2: Relative fractional abundances of different levels of ligand substitution x for each of the Cu^{2+}-ligand complexes as a function of the selected ligand concentration for (a) Br^-, (b) Cl^-, and (c) NO_2^-. Values are calculated from the analysis in Figure S1, based on data reported in Refs.[1-3]. The stability constants for the copper acetate complex were not available.

	[Ligand/[Cu^{2+}]	**0**	**1**	**10**	**100**	**500**
Br^-	$x = 0$	1	0.11	0	0	0
	$x = 1$	0	0.55	0.03	0	0
	$x = 2$	0	0.27	0.15	0	0
	$x = 3$	0	0.06	0.3	0.05	0.01
	$x = 4$	0	0.01	0.52	0.94	0.99
Cl^-	$x = 0$	1	0.31	0.01	0	0
	$x = 1$	0	0.47	0.08	0	0
	$x = 2$	0	0.2	0.32	0.02	0
	$x = 3$	0	0.03	0.44	0.21	0.05
	$x = 4$	0	0	0.16	0.77	0.95
NO_2^-	$x = 0$	0.98	0.01	0.00	0.00	0.00
	$x = 1$	0.02	0.26	0.01	0.00	0.00
	$x = 2$	0.00	0.52	0.20	0.02	0.00
	$x = 3$	0.00	0.21	0.79	0.98	1.00
	$x = 4$	0.00	0.00	0.00	0.00	0.00

Table S3: Average slopes (FWHM vs. Δ_i energy) and ranges (Δ_4 - Δ_1) in Figure 6 for each ligand species.

Substituted ligand	**Δ_4 - Δ_1(eV)**	**Fitted slope of FWHM vs. average energy**
None (H_2O)	0.42	-0.60
Br^-	0.48	-0.46
Cl^-	0.44	-0.62
Ac^-	0.42	-0.44
NO_2^-	0.72	-0.35

References

(1) Khan, M. A.; Schwing-Weill, M. J. *Bulletin de la Societe Chimique de France* **1977**, *5-6*, 399.

(2) Bjerrum, J.; Skibsted, L. H. *Acta Chemica Scandinavica Series a-Physical and Inorganic Chemistry* **1977**, *31*, 673.

(3) Kossiakoff, A.; Sickman, D. V. *Journal of the American Chemical Society* **1946**, *68*, 442.

(4) Freiser, H.; Fernando, Q. *Ionic Equilibria in Analytical Chemistry*; John Wiley & Sons, Inc: New York, 1963.