Supporting Information

Charge-Density Induced Discrimination of Halides with a Rigid Dinuclear Copper(II) Complex

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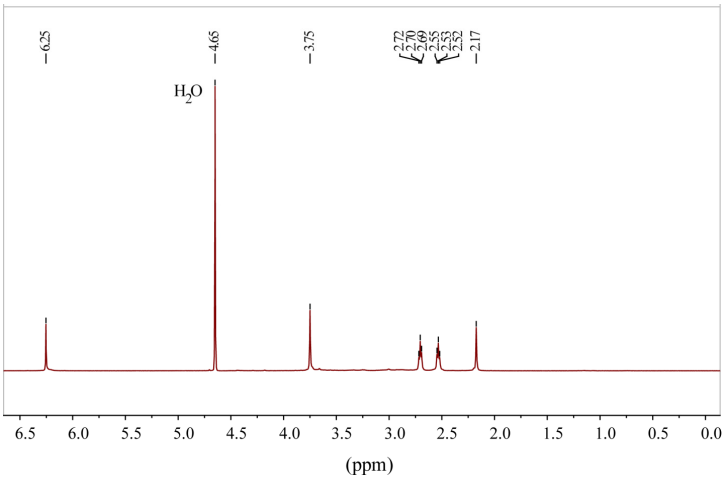

Figure S1. ^{1}H NMR (500 MHz) spectrum of **1** in D_2O.

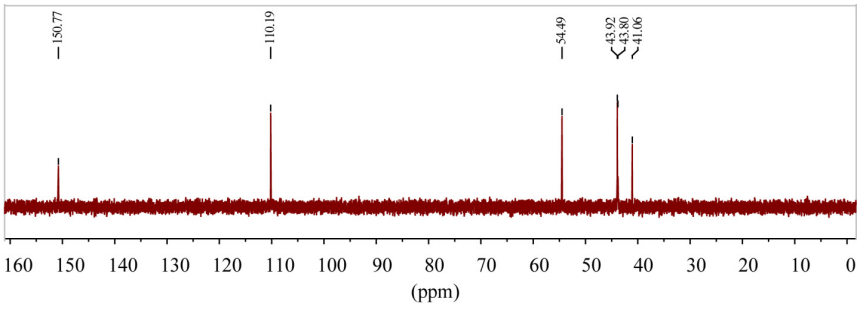

Figure S2. ^{13}C NMR (125 MHz) spectrum of **1** in D_2O.

Table S1. Crystal data and structure refinement for **L**

Empirical formula	$(C_{22}H_{38}Br_4Cu_2M_6O_2)\cdot 4(H_2O)$	
	$C_{22}H_{46}Br_4Cu_2N_6O_6$	
Formula weight	937.37	
Crystal system	monoclinic	
Space group	*P*2/*c*	
Unit cell dimensions	*a* = 8.2177(15) Å	α= 90°
	b = 8.2395(14) Å	β= 93.288(2)°
	c = 23.750(4) Å	γ= 90°
Volume	1605.5(5) $Å^3$	
Z, Z'	2, 1/2	
Density (calculated)	1.939 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	932	
Absorption coefficient	6.348 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.269 and 0.143	
Theta range for data collection	2.472 to 25.679°	
Reflections collected	16798	
Independent reflections	2921 [R(int) = 0.0569]	
Data / restraints / parameters	2921 / 18 / 205	
wR(F^2 all data)	*wR*2 = 0.1283	
R(*F* obsd data)	*R*1 = 0.0406	
Goodness-of-fit on F^2	1.005	
Observed data [I > 2σ(I)]	2500	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	0.993 and -0.786 $e/Å^3$	

$wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

$R1 = \Sigma||F_o| - |F_c||/\Sigma |F_o|$

Table S2. Hydrogen bonds for **L** [in Å and degrees].

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
C(3)-H(3A)···Br(1)#2	0.99	2.95	3.782(6)	142.1
C(3)-H(3B)···Br(1)#3	0.99	2.88	3.622(7)	132.3
N(4)-H(4)···Br(1)#3	0.87(5)	2.74(5)	3.524(5)	151(3)
C(5)-H(5B)···Br(2)	0.99	2.88	3.408(7)	114.3
C(11)-H(11A)···Br(2)#1	0.99	2.74	3.418(6)	125.8
N(12)-H(12)···Br(2)	0.87(5)	2.77(6)	3.588(5)	157(6)
C(14)-H(14A)···Br(2)#4	0.99	2.94	3.710(7)	135.3
C(14)-H(14B)···Br(2)	0.99	2.91	3.732(7)	140.9
C(15)-H(15B)···Br(1)#3	0.98	3.03	4.009(7)	178.9
O(1S)-H(1SA)···Br(1)#5	0.875(18)	2.500(19)	3.374(5)	177(7)
O(1S)-H(1SB)···O(1S)#6	0.87(2)	2.04(4)	2.819(13)	148(7)
O(1S)-H(1SC)···O(2S)	0.86(2)	1.99(4)	2.768(9)	150(8)
O(2S)-H(2SA)···Br(1)	0.862(19)	2.58(2)	3.431(5)	167(7)
O(2S)-H(2SB)···O(1S)	0.86(2)	2.05(4)	2.768(9)	141(6)
O(2S)-H(2SC)···O(2S)#3	0.86(2)	1.99(4)	2.751(15)	146(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z #2 x+1, y, z #3 -x+1, y, -z+1/2

#4 -x+1, -y, -z #5 x, y-1, z #6 -x, y, -z+1/2

Table S3. Cartesian coordinates (in Å) calculated with density functional theory (DFT) using the M06L meta-GGA functional for the fluoride complex of **L** in the gas phase.

Br	3.041700	4.613700	5.402600
Br	2.987200	2.183500	2.256900
Cu	3.988300	4.426000	2.656400
N	4.935900	6.326000	2.771100
C	6.322200	5.901300	2.508600
H	7.008300	6.765200	2.521700
H	6.318300	5.450200	1.511000
C	6.740800	4.864900	3.533900
H	7.683700	4.410100	3.212000
H	6.918200	5.309100	4.521300
N	5.694900	3.815800	3.638800
H	5.216400	3.899500	4.547400
C	6.226600	2.437900	3.564200
H	6.872500	2.220000	4.428400
H	5.351100	1.777700	3.623100
C	7.010200	2.171200	2.333800
O	6.497100	2.662200	1.176800
C	8.129000	1.438700	2.057400
H	8.749800	0.926200	2.780200
C	8.286200	1.458500	0.637900
H	9.059500	0.974500	0.057400
C	7.272000	2.227000	0.143200
C	6.850100	2.687100	-1.214300
H	7.286400	3.663800	-1.463200
H	7.211300	1.977400	-1.969200
N	5.397000	2.854500	-1.328300
H	5.145300	3.615000	-0.635900
C	4.637800	1.661300	-0.917100
H	4.719500	1.483600	0.160800
H	5.031300	0.781700	-1.442900
C	3.191000	1.917600	-1.255600
H	2.542700	1.089100	-0.928200
H	2.868500	2.817800	-0.716300
C	4.839100	7.092300	4.015400
H	5.485000	7.985300	3.960500
H	5.106300	6.479800	4.876600
H	3.804700	7.396200	4.183900
N	3.067500	2.173700	-2.703300
C	1.773800	2.775500	-3.075600
H	1.025100	1.995200	-3.282500
H	1.408500	3.356200	-2.224500
C	1.982000	3.669200	-4.283500

H	1.032700	4.127800	-4.597300
H	2.376400	3.082700	-5.121600
N	3.000000	4.682000	-3.956200
H	3.550300	4.872000	-4.795300
C	2.437300	5.973200	-3.494400
H	1.893500	6.462400	-4.316600
H	3.299800	6.596000	-3.226800
C	1.488700	5.867800	-2.366100
O	1.979200	5.469100	-1.152800
C	0.153700	6.122000	-2.249900
H	-0.494400	6.458100	-3.048700
C	-0.197500	5.883600	-0.888100
H	-1.169600	5.995900	-0.429100
C	0.941300	5.480300	-0.256500
C	1.291900	5.041100	1.125800
H	1.235500	3.947100	1.222700
H	0.580900	5.458300	1.847600
N	2.656700	5.424300	1.468100
H	3.294700	5.117200	0.701900
C	2.858400	6.868000	1.626700
H	2.406400	7.432100	0.795800
H	2.367000	7.190900	2.555300
C	4.353900	7.111200	1.661200
H	4.584600	8.180300	1.784000
H	4.793600	6.753100	0.726300
C	3.277200	0.943300	-3.474300
H	2.572800	0.163000	-3.143200
H	3.148200	1.148800	-4.537300
H	4.302200	0.588300	-3.361200
Br	5.316800	2.828200	-5.374700
Br	5.813700	5.753400	-2.714700
Cu	4.556900	3.650200	-2.975200
F	4.775100	4.600600	0.461300

Table S4. Cartesian coordinates (in Å) calculated with density functional theory (DFT) using the M06L meta-GGA functional for the chloride complex of **L** in the gas phase.

Br	3.238900	6.521600	5.512900
Br	2.080700	3.404300	4.183900
Cu	3.678500	5.103400	3.461000
N	5.325100	6.290200	2.775800
C	6.577700	5.576800	3.128200
H	7.400500	6.294900	3.255500
H	6.850500	4.922700	2.298700
C	6.374300	4.771700	4.401300
H	7.298800	4.233100	4.661300
H	6.129400	5.452100	5.226100
N	5.220100	3.880000	4.237800
H	4.766800	3.744300	5.139200
C	5.488200	2.520000	3.705700
H	5.948100	1.891000	4.482100
H	4.503500	2.098100	3.456800
C	6.384100	2.453800	2.533700
O	5.955500	3.004200	1.361600
C	7.596300	1.858400	2.336200
H	8.170700	1.335200	3.088900
C	7.923100	2.033400	0.959400
H	8.803000	1.682000	0.438300
C	6.898200	2.742000	0.404400
C	6.589800	3.285300	-0.938600
H	6.528000	4.380000	-0.914100
H	7.389500	3.034200	-1.643100
N	5.308000	2.791000	-1.479500
H	4.606900	2.795600	-0.712100
C	5.411200	1.395600	-1.938900
H	5.835100	0.747100	-1.157100
H	6.088000	1.378600	-2.805600
C	4.025100	0.926100	-2.312500
H	4.051100	-0.083800	-2.741800
H	3.404600	0.907000	-1.410300
C	5.376400	7.649700	3.331500
H	6.186200	8.218800	2.849000
H	5.529100	7.603600	4.409800
H	4.425200	8.160700	3.175700
N	3.429600	1.879700	-3.282300
C	2.044200	2.227600	-2.914300
H	1.387700	1.343800	-2.981400
H	2.061600	2.550800	-1.864000
C	1.534300	3.346400	-3.793400
H	0.583100	3.708000	-3.387900

H	1.337300	3.006200	-4.817500
N	2.524100	4.449300	-3.798800
H	2.925700	4.538100	-4.733800
C	1.934700	5.763900	-3.470300
H	1.214400	6.078300	-4.242100
H	2.768300	6.477200	-3.471800
C	1.211300	5.812200	-2.178700
O	1.821400	5.322700	-1.058000
C	0.040900	6.421800	-1.832400
H	-0.647600	6.899400	-2.516800
C	-0.058200	6.340700	-0.414700
H	-0.843800	6.731000	0.217100
C	1.041300	5.657600	0.015800
C	1.494100	5.245300	1.371600
H	1.209400	4.210300	1.598200
H	1.002500	5.886100	2.112900
N	2.952300	5.297000	1.565800
H	3.308000	4.473200	1.054400
C	3.603400	6.517000	1.059300
H	3.438400	6.667000	-0.011200
H	3.184600	7.376600	1.600200
C	5.081300	6.364800	1.315900
H	5.660800	7.174600	0.847800
H	5.415600	5.427800	0.858100
C	3.512900	1.327800	-4.635200
H	2.876300	0.431800	-4.724300
H	3.219200	2.069100	-5.380000
H	4.550700	1.077000	-4.859300
Br	5.610300	3.828600	-5.261400
Br	5.076200	6.038400	-2.201100
Cu	4.380100	3.772900	-2.997100
Cl	2.908200	2.260900	0.587100

Table S5. Cartesian coordinates (in Å) calculated with density functional theory (DFT) using the M06L meta-GGA functional for the bromide complex of **L** in the gas phase.

Br	2.615400	6.992500	4.771400
Br	2.152600	3.491700	4.405600
Cu	3.723200	5.147900	3.499100
N	5.391300	6.318300	2.796100
C	6.630400	5.583700	3.142500
H	7.471500	6.282100	3.261600
H	6.885600	4.917400	2.318000
C	6.420600	4.789000	4.420600
H	7.322400	4.203200	4.655900
H	6.240100	5.476400	5.255700
N	5.222200	3.950200	4.283000
H	4.791200	3.806200	5.193300
C	5.435200	2.578500	3.737000
H	5.880500	1.937100	4.510700
H	4.433600	2.190000	3.498800
C	6.316500	2.486100	2.558700
O	5.901900	3.061700	1.394000
C	7.499100	1.838400	2.347900
H	8.055900	1.286200	3.093100
C	7.819800	2.003600	0.969000
H	8.677000	1.613800	0.437600
C	6.822500	2.759100	0.426300
C	6.517900	3.309400	-0.912500
H	6.424900	4.401100	-0.874300
H	7.331800	3.090600	-1.610800
N	5.258600	2.786800	-1.483900
H	4.552100	2.740000	-0.724000
C	5.421000	1.410100	-1.983900
H	5.843200	0.751300	-1.210000
H	6.119400	1.446100	-2.832300
C	4.063100	0.907400	-2.410400
H	4.138600	-0.078200	-2.885900
H	3.428600	0.817600	-1.521000
C	5.466200	7.673000	3.358500
H	6.336400	8.203200	2.940500
H	5.544300	7.625600	4.446500
H	4.551600	8.223400	3.138800
N	3.445600	1.881600	-3.346800
C	2.066800	2.211500	-2.937600
H	1.418300	1.321600	-2.996400
H	2.106400	2.517300	-1.882600
C	1.519800	3.336600	-3.784700
H	0.580000	3.684900	-3.342800

H	1.291500	3.007400	-4.805800
N	2.499500	4.448000	-3.805500
H	2.873600	4.549100	-4.749300
C	1.905000	5.754500	-3.450200
H	1.165600	6.070300	-4.203100
H	2.731800	6.475400	-3.460000
C	1.208800	5.775000	-2.144000
O	1.854400	5.287800	-1.041800
C	0.030400	6.349000	-1.766500
H	-0.683300	6.817600	-2.431200
C	-0.039500	6.245700	-0.348500
H	-0.820800	6.608600	0.304300
C	1.085500	5.587100	0.052100
C	1.587400	5.172800	1.389400
H	1.316400	4.134800	1.622900
H	1.123000	5.808900	2.154100
N	3.046700	5.241000	1.537600
H	3.426700	4.444800	1.009900
C	3.654000	6.499700	1.077500
H	3.482900	6.689100	0.013300
H	3.201000	7.315100	1.659900
C	5.138900	6.406200	1.334900
H	5.681300	7.251100	0.885500
H	5.518800	5.495600	0.860100
C	3.498700	1.362900	-4.714400
H	2.857500	0.471300	-4.812900
H	3.190200	2.122600	-5.434400
H	4.531200	1.116400	-4.965000
Br	5.671700	3.817000	-5.241800
Br	5.065100	6.041100	-2.241400
Cu	4.377300	3.777300	-3.030800
Br	2.846600	1.886400	0.762800

Table S6. Cartesian coordinates (in Å) calculated with density functional theory (DFT) using the M06L meta-GGA functional for the iodide complex of **L** in the gas phase.

Br	0.962000	6.321900	4.073300
Br	3.106000	3.859400	5.291500
Cu	2.776200	4.865800	3.122800
N	4.722200	6.096900	3.028500
C	6.099600	5.554600	3.012300
H	6.802800	6.402000	3.134400
H	6.270700	5.121800	2.020500
C	6.400300	4.478700	4.047000
H	7.495100	4.437200	4.165600
H	5.994300	4.770400	5.025600
N	5.893500	3.180500	3.663300
H	5.128300	2.879600	4.254600
C	6.848800	2.138100	3.408800
H	7.649000	2.039000	4.173600
H	6.294700	1.188800	3.424900
C	7.527500	2.274400	2.088700
O	6.738000	2.662300	1.046900
C	8.780900	2.002600	1.623700
H	9.619600	1.673200	2.222200
C	8.754500	2.215400	0.210700
H	9.570300	2.101100	-0.489700
C	7.490700	2.625100	-0.091900
C	6.777800	3.121200	-1.295200
H	6.767100	4.218400	-1.322600
H	7.257800	2.786900	-2.220800
N	5.365100	2.696200	-1.323800
H	4.953900	2.942200	-0.415600
C	5.210100	1.244200	-1.508200
H	5.650500	0.680200	-0.673600
H	5.754500	0.979200	-2.425300
C	3.731600	0.945700	-1.631000
H	3.545200	-0.131000	-1.757300
H	3.231700	1.257700	-0.708400
C	4.536600	6.945800	4.211600
H	5.326700	7.715700	4.267100
H	4.548700	6.339100	5.120000
H	3.558000	7.431700	4.174000
N	3.168800	1.719900	-2.750600
C	1.808300	2.204300	-2.493700
H	1.079100	1.376600	-2.447600
H	1.817000	2.696900	-1.512500
C	1.408000	3.206300	-3.562900
H	0.528500	3.758500	-3.221500

H	1.129600	2.704300	-4.498800
N	2.525500	4.148500	-3.799700
H	3.000700	3.899100	-4.670500
C	2.118000	5.549000	-3.941900
H	1.448700	5.683300	-4.808000
H	3.035700	6.115400	-4.149300
C	1.460400	6.108400	-2.729300
O	1.542400	5.401400	-1.571700
C	0.846200	7.304700	-2.501300
H	0.648200	8.068800	-3.240100
C	0.575600	7.355900	-1.104800
H	0.119800	8.163300	-0.548400
C	1.018300	6.180900	-0.572400
C	1.137500	5.655300	0.799200
H	0.823700	4.606700	0.859600
H	0.517600	6.233000	1.488600
N	2.532400	5.694200	1.319500
H	3.106500	5.156700	0.657400
C	3.105400	7.049200	1.398000
H	3.056600	7.542300	0.416100
H	2.500400	7.617600	2.114600
C	4.551700	6.912100	1.807000
H	5.017200	7.904200	1.930000
H	5.079700	6.410100	0.989200
C	3.256000	0.956400	-3.992500
H	2.568000	0.093400	-3.977000
H	3.034300	1.584500	-4.858700
H	4.280100	0.606100	-4.136100
Br	5.562200	3.344100	-4.904100
Br	4.684000	5.852500	-1.663300
Cu	4.225700	3.622100	-2.704300
I	2.702600	2.455800	1.771200