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Supporting information

The unprecedented interplay of antiferro- and ferromagnetic exchange interactions through intermolecular hydrogen bonds in mononuclear Cu(II) complexes.

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Table S1. Selected bond distances (Å) and angles (°) for **I** and **II** (Hal = Br in **I** and Cl in **II**).

Compound	I	II
Cu1—Hal1	2.5741(6)	2.4587(16)
Cu1—Hal2	2.3920(6)	2.2812(16)
Cu1—N1	2.028(3)	2.053(5)
Cu1—N2	1.983(3)	2.020(4)
Cu1—N4	2.042(2)	2.094(5)
O1—N1	1.384(3)	1.412(6)
N1—C1	1.285(4)	1.294(7)
C1—C2	1.485(4)	1.495(8)
N2—C2	1.289(4)	1.282(8)
N2—N3	1.345(3)	1.361(7)
N3—C3	1.373(4)	1.394(7)
N4—C3	1.342(4)	1.359(7)
N5—C3	1.330(4)	1.349(7)
N4—C4	1.362(4)	1.380(8)
C4—C5	1.379(4)	1.396(8)
N5—C6	1.347(4)	1.326(8)
C5—C6	1.381(5)	1.419(8)
Hal1—Cu1—Hal2	108.63(2)	99.95(6)
N1—Cu1—Hal2	90.87(8)	89.96(13)
N4—Cu1—Hal2	106.96(7)	111.21(14)
N1—Cu1—N2	76.46(10)	76.18(19)
N2—Cu1—N4	79.68(10)	78.93(19)
O1—N1—C1	115.7(3)	115.1(5)
N1—C1—C2	113.2(3)	112.2(5)
C1—C2—N2	112.3(3)	114.3(5)
C2—N2—N3	125.4(3)	126.1(5)
N2—N3—C3	115.8(3)	115.5(5)
N3—C3—N4	117.5(3)	117.9(5)
N3—C3—N5	114.7(3)	114.9(5)
C3—N4—C4	115.7(3)	116.0(5)
C3—N5—C6	115.8(3)	116.4(5)
N4—C3—N5	127.8(3)	127.2(6)

Table S2 . Exchange interaction parameter in dimers of **Ib** type, calculated with B3LYP functional (ORCA code) and different basis sets and the corresponding number of basis functions.

Basis set	Number of basis functions	-2J, cm ⁻¹
6-311G(d)	982	+0.27
6-311+G(d,p)	1260	+0.33
6-311++G(d,p)	1294	+0.33
TZVP	1060	+0.33
TZVPP	1802	+0.27
def2-TZVPPD	2210	+0.29

Table S3. Atomic coordinates of the dimers **Ia**, **Ib**, **IIa** – **IIc** exploited for the calculation of intermolecular exchange interactions

Dimer Ia

29	0.004460000	0.005653000	0.000002000
35	0.450383000	-2.484972000	0.473761000
35	0.209794000	0.384802000	-2.352882000
8	2.982732000	0.385004000	-0.575714000
1	2.489835000	0.209406000	-1.425194000
7	1.924217000	0.589030000	0.292861000
7	-0.036060000	0.853308000	1.792506000
7	-1.261399000	0.971201000	2.333613000
1	-1.481540000	1.332308000	3.300527000
7	-1.992060000	-0.107885000	0.413501000
7	-3.471048000	0.439352000	2.220762000
6	2.238169000	1.039115000	1.454430000
6	1.061277000	1.257293000	2.333804000
6	-2.286796000	0.409305000	1.615845000
6	-3.030390000	-0.679875000	-0.255971000
6	-4.300981000	-0.652279000	0.281777000
1	-5.125577000	-1.106913000	-0.266049000
6	-4.494942000	-0.104082000	1.534703000
6	3.618502000	1.372165000	1.910525000
1	3.864894000	0.768767000	2.797148000
1	4.350054000	1.169451000	1.123016000
1	3.686446000	2.432594000	2.196426000
6	1.174783000	1.922720000	3.661586000
1	2.123834000	1.658966000	4.144928000
1	1.160713000	3.020237000	3.551547000
1	0.362118000	1.664606000	4.351296000
6	-2.742211000	-1.379398000	-1.545162000
1	-2.247057000	-0.701916000	-2.256483000
1	-2.022587000	-2.193100000	-1.358336000
1	-3.660067000	-1.787241000	-1.982839000
6	-5.809008000	-0.147433000	2.249827000
1	-5.967926000	0.776533000	2.820633000
1	-5.811062000	-0.981006000	2.970203000

8	-2.211659000	1.657964000	4.790385000
1	-1.722915000	1.997172000	5.601247000
1	-3.027263000	2.181692000	4.727267000
8	2.210982000	-1.658401000	3.064888000
1	1.732474000	-2.005891000	2.251828000
1	3.040740000	-2.158840000	3.130481000
29	-0.005137000	-0.006089000	7.855270000
35	-0.451061000	2.484535000	7.381511000
35	-0.210472000	-0.385238000	10.208156000
8	-2.983409000	-0.385440000	8.430987000
1	-2.490577000	-0.211861000	9.280922000
7	-1.924894000	-0.589465000	7.562412000
7	0.035383000	-0.853745000	6.062766000
7	1.260722000	-0.971636000	5.521661000
1	1.480702000	-1.335255000	4.555870000
7	1.991383000	0.107449000	7.441773000
7	3.470370000	-0.439788000	5.634512000
6	-2.238845000	-1.039550000	6.400843000
6	-1.061954000	-1.257728000	5.521469000
6	2.286119000	-0.409742000	6.239427000
6	3.029713000	0.679439000	8.111244000
6	4.300304000	0.651843000	7.573495000
1	5.124913000	1.106497000	8.121266000
6	4.494265000	0.103645000	6.320570000
6	-3.619179000	-1.372600000	5.944748000
1	-3.883765000	-0.730621000	5.090698000
1	-4.344811000	-1.217223000	6.748399000
1	-3.673998000	-2.418567000	5.608709000
6	-1.175459000	-1.923156000	4.193688000
1	-2.122257000	-1.655572000	3.708146000
1	-1.166465000	-3.020669000	4.304174000
1	-0.359949000	-1.668329000	3.506133000
6	2.741534000	1.378961000	9.400435000
1	2.246228000	0.701515000	10.111688000
1	2.022017000	2.192746000	9.213546000
1	3.659397000	1.786685000	9.838201000
6	5.808331000	0.146996000	5.605446000
1	5.969750000	-0.779272000	5.039017000
1	6.647018000	0.305421000	6.295006000
1	5.808417000	0.977002000	4.880958000
1	-6.648194000	-0.300599000	1.559642000

Dimer Ib

29	0.793331000	9.775873000	7.922609000
35	-0.892624000	11.609619000	7.273429000
35	2.457252000	10.737097000	9.347179000
8	-0.361896000	9.776012000	10.752962000
1	0.402645000	10.409818000	10.699736000
7	-0.256728000	9.130614000	9.532756000
7	-0.037578000	8.089896000	7.289914000
7	0.350361000	7.694498000	6.064633000
1	-0.086218000	6.914039000	5.526886000

7	1.611217000	9.642649000	6.056253000
7	1.466999000	8.198110000	4.146917000
6	-1.035416000	8.121981000	9.369391000
6	-0.863088000	7.458612000	8.051735000
6	1.185473000	8.554387000	5.397150000
6	2.416181000	10.484733000	5.351682000
6	2.792522000	10.166864000	4.062626000
1	3.418813000	10.858889000	3.499801000
6	2.287669000	9.025269000	3.471146000
6	-1.997174000	7.597083000	10.381205000
1	-2.965439000	8.115516000	10.291709000
1	-1.627113000	7.782161000	11.397495000
1	-2.173643000	6.524347000	10.245190000
6	-1.544751000	6.178505000	7.712115000
1	-2.639517000	6.288477000	7.759115000
1	-1.273036000	5.387181000	8.427175000
1	-1.283675000	5.826784000	6.708609000
6	2.824503000	11.773230000	5.989993000
1	3.417638000	11.588632000	6.895998000
1	1.919483000	12.307093000	6.325435000
1	3.391449000	12.394847000	5.287298000
6	2.535953000	8.670442000	2.038490000
1	2.642162000	7.584043000	1.920320000
1	3.411099000	9.189999000	1.628852000
1	1.658500000	8.972385000	1.442964000
29	3.935882000	5.512375000	4.085551000
35	5.621838000	3.678628000	4.734732000
35	2.271962000	4.551150000	2.660982000
8	5.091110000	5.512235000	1.255198000
1	4.326592000	4.878368000	1.308451000
7	4.985942000	6.157634000	2.475404000
7	4.766791000	7.198352000	4.718246000
7	4.378853000	7.593750000	5.943527000
1	4.818904000	8.370916000	6.483137000
7	3.117996000	5.645598000	5.951907000
7	3.262214000	7.090138000	7.861245000
6	5.764630000	7.166266000	2.638770000
6	5.592302000	7.829636000	3.956425000
6	3.543741000	6.733861000	6.611010000
6	2.313033000	4.803515000	6.656478000
6	1.936692000	5.121384000	7.945534000
1	1.313079000	4.427776000	8.509413000
6	2.441544000	6.262978000	8.537014000
6	6.726388000	7.691165000	1.626955000
1	7.691602000	7.166098000	1.710157000
1	6.352002000	7.513994000	0.610750000
1	6.909752000	8.761956000	1.768360000
6	6.273964000	9.109743000	4.296045000
1	7.368938000	8.996580000	4.261959000
1	6.012031000	9.897606000	3.573681000
1	6.002371000	9.468050000	5.294460000
6	1.904711000	3.515017000	6.018168000

1	1.319563000	3.699376000	5.106964000
1	2.810391000	2.977081000	5.690978000
1	1.330148000	2.897094000	6.717964000
6	2.193261000	6.617806000	9.969671000
1	2.087322000	7.704229000	10.087872000
1	1.317961000	6.098442000	10.379228000
1	3.070617000	6.315680000	10.565254000
8	-0.482735000	5.780752000	4.317092000
1	-0.975534000	4.957285000	4.166705000
1	0.314754000	5.712127000	3.736911000
8	5.211948000	9.507495000	7.691068000
1	5.714561000	10.323644000	7.848071000
1	4.414052000	9.580532000	8.270038000

Dimer IIa

29	3.786636000	13.606362000	5.791740000
17	4.924237000	14.373407000	7.832061000
17	5.583464000	13.356046000	4.408744000
8	4.818090000	10.675147000	5.837549000
1	5.406709000	11.244252000	5.263895000
7	3.787468000	11.587247000	6.156660000
7	1.994739000	13.271480000	6.661407000
7	1.188278000	14.362573000	6.766801000
1	0.327142000	14.398460000	7.307862000
7	2.836364000	15.444036000	5.472698000
7	0.842768000	16.588587000	6.246900000
6	2.827501000	11.100977000	6.875004000
6	1.764294000	12.113357000	7.155857000
6	1.639383000	15.509053000	6.113321000
6	3.284843000	16.623026000	4.911899000
6	2.512921000	17.783626000	5.003606000
1	2.860964000	18.714928000	4.561324000
6	1.282400000	17.716618000	5.706138000
6	2.784751000	9.695039000	7.411478000
1	3.217458000	9.003925000	6.677355000
1	1.761273000	9.383225000	7.648916000
1	3.395056000	9.625241000	8.325513000
6	0.566850000	11.745265000	7.984973000
1	-0.012193000	12.622248000	8.300472000
1	0.879139000	11.218732000	8.897353000
1	-0.110169000	11.076207000	7.430693000
6	4.610813000	16.606648000	4.200353000
1	5.401587000	16.312672000	4.907067000
1	4.833577000	17.593676000	3.778901000
1	4.616439000	15.845486000	3.407856000
6	0.384327000	18.9444441000	5.887760000
1	-0.661168000	18.671606000	5.693423000
1	0.685220000	19.764687000	5.225280000
1	0.448268000	19.291481000	6.930120000
29	9.364224000	9.562638000	3.297266000
17	8.226625000	8.795593000	1.256944000
17	7.567398000	9.812955000	4.680262000
8	8.332771000	12.493853000	3.251457000

1	7.744153000	11.924748000	3.825111000
7	9.363394000	11.581753000	2.932346000
7	11.156122000	9.897520000	2.427599000
7	11.962584000	8.806427000	2.322205000
1	12.823719000	8.770540000	1.781143000
7	10.314498000	7.724964000	3.616308000
7	12.308094000	6.580413000	2.842106000
6	10.323360000	12.068023000	2.214002000
6	11.386567000	11.055643000	1.933149000
6	11.511478000	7.659947000	2.975685000
6	9.866018000	6.545973000	4.177107000
6	10.637940000	5.385374000	4.085400000
1	10.289897000	4.454071000	4.527682000
6	11.868462000	5.452382000	3.382868000
6	10.366111000	13.473961000	1.677527000
1	9.933400000	14.165075000	2.411648000
1	11.389590000	13.785776000	1.440093000
1	9.755810000	13.543757000	0.763489000
6	12.584012000	11.423735000	1.104033000
1	13.163052000	10.546751000	0.788531000
1	12.271723000	11.950271000	0.191654000
1	13.261032000	12.092789000	1.658315000
6	8.540048000	6.562352000	4.888652000
1	7.749274000	6.856328000	4.181939000
1	8.317283000	5.575325000	5.310106000
1	8.534422000	7.323515000	5.681149000
6	12.766534000	4.224559000	3.201246000
1	13.812029000	4.497394000	3.395577000
1	12.465644000	3.404315000	3.863730000
1	12.702588000	3.877515000	2.158888000

Dimer IIb

29	3.786157000	13.602997000	5.792954000
17	4.924574000	14.373135000	7.831654000
17	5.582267000	13.352138000	4.409125000
8	4.819416000	10.672463000	5.841569000
1	5.388793000	11.219916000	5.221141000
7	3.788442000	11.584314000	6.160252000
7	1.995010000	13.268056000	6.664142000
7	1.187954000	14.358784000	6.768757000
1	0.389138000	14.425335000	7.402593000
7	2.834571000	15.439718000	5.472344000
7	0.840768000	16.583974000	6.246450000
6	2.829221000	11.098311000	6.879773000
6	1.765577000	12.110377000	7.160101000
6	1.637954000	15.504765000	6.113643000
6	3.281983000	16.618317000	4.909875000
6	2.509415000	17.778557000	5.000699000
1	2.855986000	18.712377000	4.553157000
6	1.279376000	17.711633000	5.704083000
6	2.787660000	9.692980000	7.417930000
1	3.695606000	9.153759000	7.117838000
1	1.911439000	9.140992000	7.032583000

1	2.722887000	9.699745000	8.520562000
6	0.568878000	11.742538000	7.990403000
1	0.692550000	12.076256000	9.038791000
1	0.410432000	10.654782000	8.005536000
1	-0.353932000	12.207186000	7.596543000
6	4.607516000	16.601903000	4.197515000
1	5.418542000	16.400516000	4.922583000
1	4.792087000	17.567895000	3.702735000
1	4.649572000	15.786119000	3.457226000
6	0.380674000	18.939125000	5.884823000
1	-0.664765000	18.676304000	5.655249000
1	0.700465000	19.775075000	5.243511000
1	0.413714000	19.270906000	6.937819000
29	10.657853000	13.609309000	5.789200000
17	11.796271000	14.379447000	7.827899000
17	12.453963000	13.358450000	4.405370000
8	11.691112000	10.678775000	5.837814000
1	12.294436000	11.250544000	5.282347000
7	10.660138000	11.590626000	6.156498000
7	8.866706000	13.274368000	6.660388000
7	8.059650000	14.365096000	6.765002000
1	7.072932000	14.333210000	7.112655000
7	9.706267000	15.446030000	5.468590000
7	7.712464000	16.590286000	6.242696000
6	9.700917000	11.104623000	6.876018000
6	8.637273000	12.116689000	7.156346000
6	8.509650000	15.511077000	6.109888000
6	10.153679000	16.624629000	4.906120000
6	9.381111000	17.784869000	4.996944000
1	9.733096000	18.719348000	4.553122000
6	8.151073000	17.717945000	5.700329000
6	9.659356000	9.699292000	7.414176000
1	10.140188000	9.015233000	6.699219000
1	8.624120000	9.376359000	7.588975000
1	10.223860000	9.645317000	8.364237000
6	7.440574000	11.748850000	7.986649000
1	6.800524000	12.611759000	8.226806000
1	7.769290000	11.283303000	8.933144000
1	6.814860000	11.015105000	7.446548000
6	11.479212000	16.608215000	4.193761000
1	12.277962000	16.317215000	4.898858000
1	11.704616000	17.599167000	3.769661000
1	11.488406000	15.851291000	3.392793000
6	7.252370000	18.945437000	5.881069000
1	6.290587000	18.636082000	6.314651000
1	7.086562000	19.464138000	4.920669000
1	7.731033000	19.667438000	6.567427000

Dimer IIc

29	9.364627000	9.559712000	3.299740000
17	8.226211000	8.789574000	1.261039000
17	7.568519000	9.810571000	4.683569000
8	8.331369000	12.490246000	3.251126000

1	7.727873000	11.918263000	3.806190000
7	9.362343000	11.578395000	2.932442000
7	11.155775000	9.894654000	2.428552000
7	11.962832000	8.803926000	2.323937000
1	12.950773000	8.836996000	1.979603000
7	10.316215000	7.722992000	3.620350000
7	12.310017000	6.578736000	2.846244000
6	10.321563000	12.064399000	2.212922000
6	11.385208000	11.052333000	1.932593000
6	11.512831000	7.657944000	2.979051000
6	9.868802000	6.544392000	4.182819000
6	10.641369000	5.384153000	4.091995000
1	10.289395000	4.449675000	4.535828000
6	11.871409000	5.451077000	3.388611000
6	10.363126000	13.469729000	1.674763000
1	9.855078000	14.149255000	2.374765000
1	11.400052000	13.802596000	1.529966000
1	9.826903000	13.516924000	0.708055000
6	12.581908000	11.420172000	1.102291000
1	13.203408000	10.551556000	0.835573000
1	12.254807000	11.915962000	0.171003000
1	13.225691000	12.128163000	1.655613000
6	8.543269000	6.560806000	4.895179000
1	7.744576000	6.852140000	4.190150000
1	8.317712000	5.569716000	5.318880000
1	8.533852000	7.317343000	5.696508000
6	12.770111000	4.223585000	3.207871000
1	13.731880000	4.532999000	2.774303000
1	12.935900000	3.704900000	4.168284000
1	12.291477000	3.501553000	2.521528000
29	10.657853000	13.609309000	5.789200000
17	11.796271000	14.379447000	7.827899000
17	12.453963000	13.358450000	4.405370000
8	11.691112000	10.678775000	5.837814000
1	12.294436000	11.250544000	5.282347000
7	10.660138000	11.590626000	6.156498000
7	8.866706000	13.274368000	6.660388000
7	8.059650000	14.365096000	6.765002000
1	7.072932000	14.333210000	7.112655000
7	9.706267000	15.446030000	5.468590000
7	7.712464000	16.590286000	6.242696000
6	9.700917000	11.104623000	6.876018000
6	8.637273000	12.116689000	7.156346000
6	8.509650000	15.511077000	6.109888000
6	10.153679000	16.624629000	4.906120000
6	9.381111000	17.784869000	4.996944000
1	9.733096000	18.719348000	4.553122000
6	8.151073000	17.717945000	5.700329000
6	9.659356000	9.699292000	7.414176000
1	10.140188000	9.015233000	6.699219000
1	8.624120000	9.376359000	7.588975000
1	10.223860000	9.645317000	8.364237000

6	7.440574000	11.748850000	7.986649000
1	6.800524000	12.611759000	8.226806000
1	7.769290000	11.283303000	8.933144000
1	6.814860000	11.015105000	7.446548000
6	11.479212000	16.608215000	4.193761000
1	12.277962000	16.317215000	4.898858000
1	11.704616000	17.599167000	3.769661000
1	11.488406000	15.851291000	3.392793000
6	7.252370000	18.945437000	5.881069000
1	6.290587000	18.636082000	6.314651000
1	7.086562000	19.464138000	4.920669000
1	7.731033000	19.667438000	6.567427000

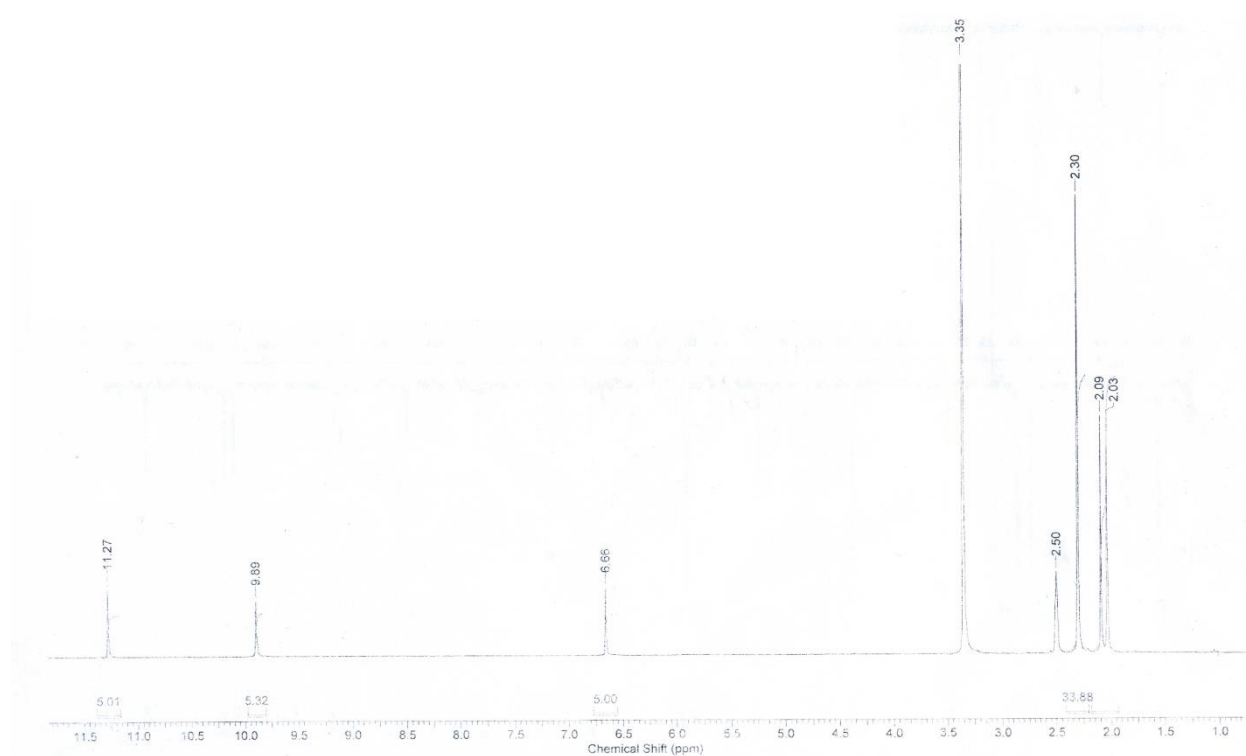


Figure S1. ^1H NMR spectrum of H_2L (DMSO-d_6 , 300 MHz)