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Electronic Supporting Information

Copper (II) dimers stabilized by bis(phenol) amine ligands: Theoretical and Experimental Insights

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Figures and Tables

Fig. S1 Absorption spectra of [$^1L_2Cu^{II}_2$] (**1**) in CH_2Cl_2 solution.

Fig. S2 Absorption spectra of [$^2L_2Cu^{II}_2$] (**1**) in CH_2Cl_2 solution.

Fig. S3 Spectral change of the titration of [$^3L_2Cu^{II}_2$] [29] (2.5×10^{-4} M) by pyridine (0 – 0.004 M) in CH_2Cl_2. Inset: plot of $(A - A_o)^2/(A - A_\infty)$ vs. [pyridine]$_2$ for the titration.

Fig. S4 Spectral change of the titration of [$^2L_2Cu^{II}_2$] (2.5×10^{-4} M) by pyridine (0 – 0.004 M) in CH_2Cl_2. Inset: plot of $(A - A_o)^2/(A - A_\infty)$ vs. [pyridine]$_2$ for the titration.

Fig. S5 ESR spectrum of [$^1L_2Cu^{II}_2$] (**1**) in CH_2Cl_2 solution at 77 K; microwave frequency 9.448 GHz, modulation frequency 100 kHz, modulation amplitude 5 G, microwave power 6.36 mW.

Fig. S6 ESR spectrum of [$^2LCu^{II}$(py)] generated from the dimer (10^{-3} M) by adding pyridine (1.6×10^{-2} M) in CH_2Cl_2 at 77 K; microwave frequency 9.448 GHz, modulation frequency 100 kHz, modulation amplitude 5 G, microwave power 6.36 mW. (C) The computer simulation spectrum with the parameters $g_1 = 2.275$, $g_2 = 2.070$, $g_3 = 2.045$, $A_1 = 160$, $A_2 = 25$, and $A_3 = 18$ G (Cu, I = 3/2); and $A_1 = A_2 = A_3 = 14$ G (N, I=1).

Fig. S7 Cyclic voltammogram (100 mV/s) of a ~1.0 mM solution of (**2**) at a platinum electrodein CH_3CN (0.1 M in TBAP).

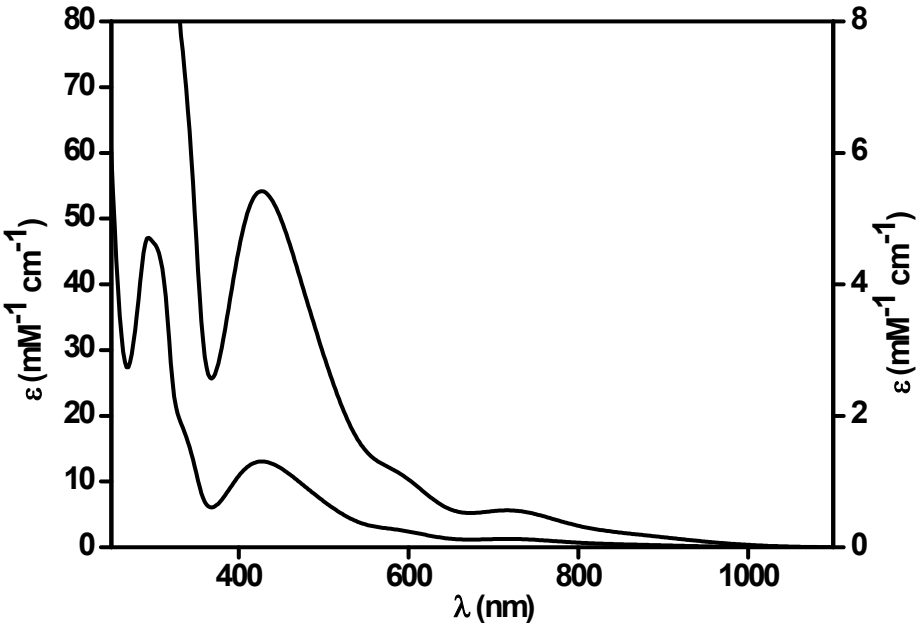
Fig. S8 *(a)* Spin-Density plot and *(b)* Magnetic orbitals for [$^1LCu^{II}Py$] (**4**) ($M_s = ½$).

Fig. S9 *(a)* Spin-Density plot and *(b)* Magnetic orbitals for [$^2LCu^{II}Py$] (**5**) ($M_s = ½$).

Fig. S10 TD-DFT calculated electronic spectra for [$^1L_2Cu^{II}_2$] (1).

Fig. S11 Representative molecular-orbitals involved in TD-DFT transitions of [(^1L)$_2Cu^{II}_2$] (**1**)**.**

Fig. S12 TD-DFT calculated electronic spectra for [(^2L)$_2Cu^{II}_2$] (**2**)**.**



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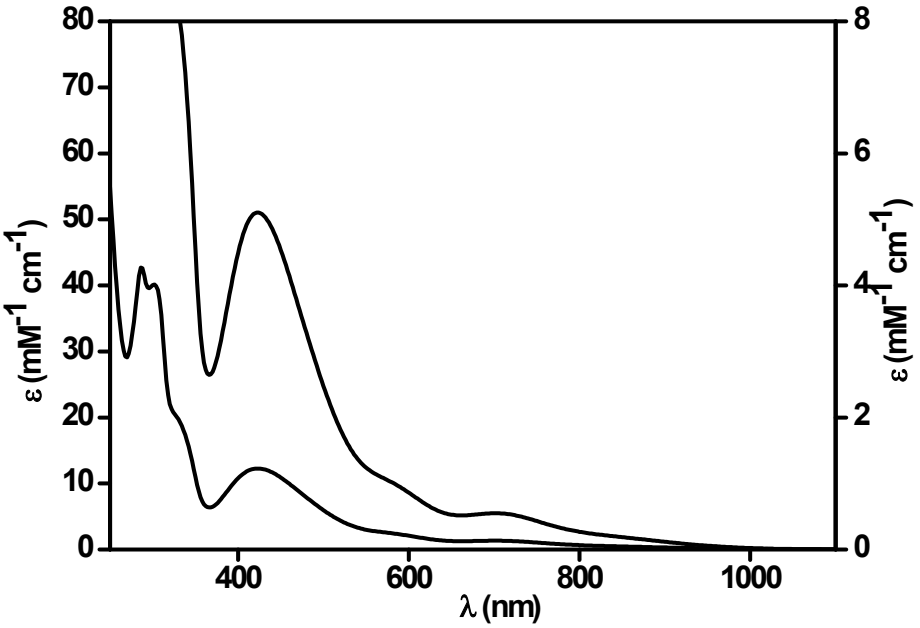
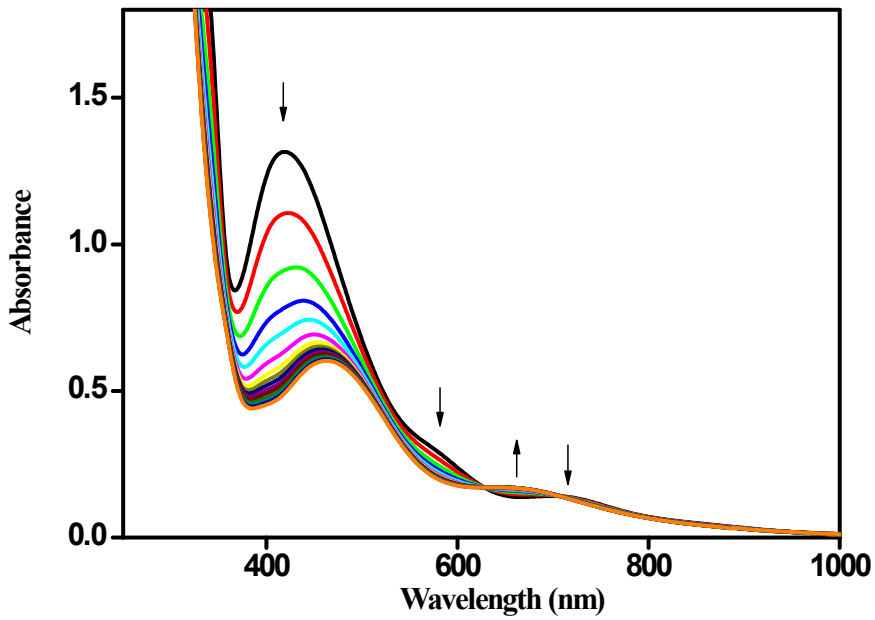


Fig. S2. Absorption spectra of $[^{2}L_2Cu^{II}_2]$ (**2**) in CH_2Cl_2 solution.



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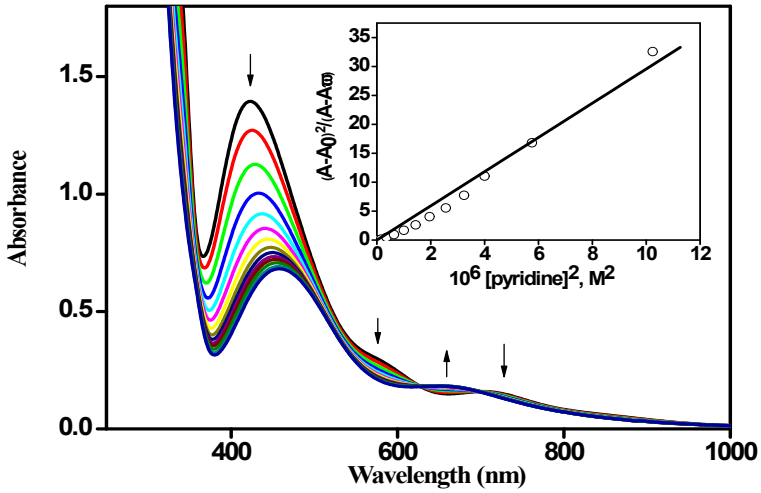

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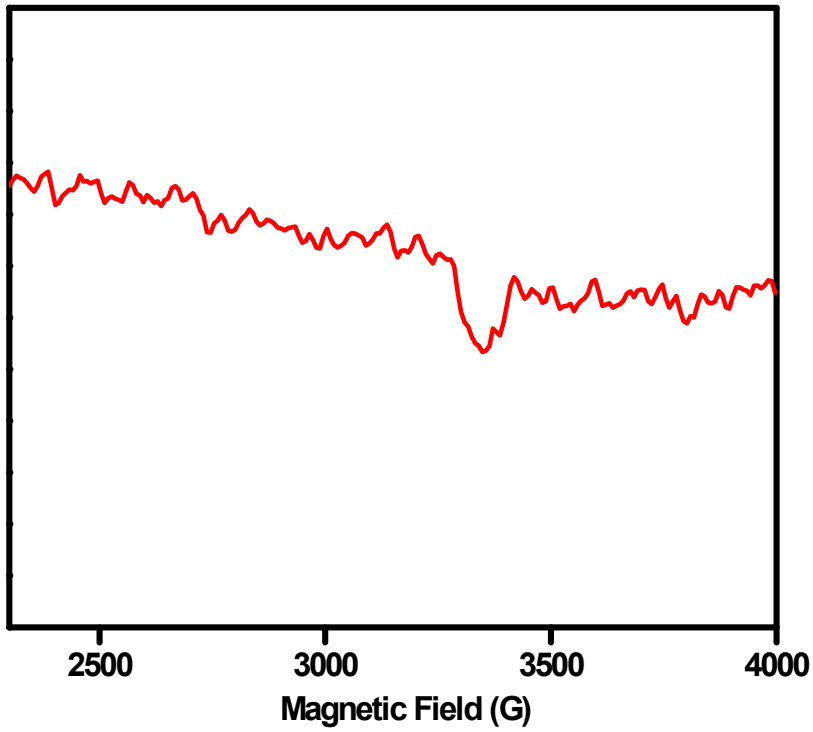

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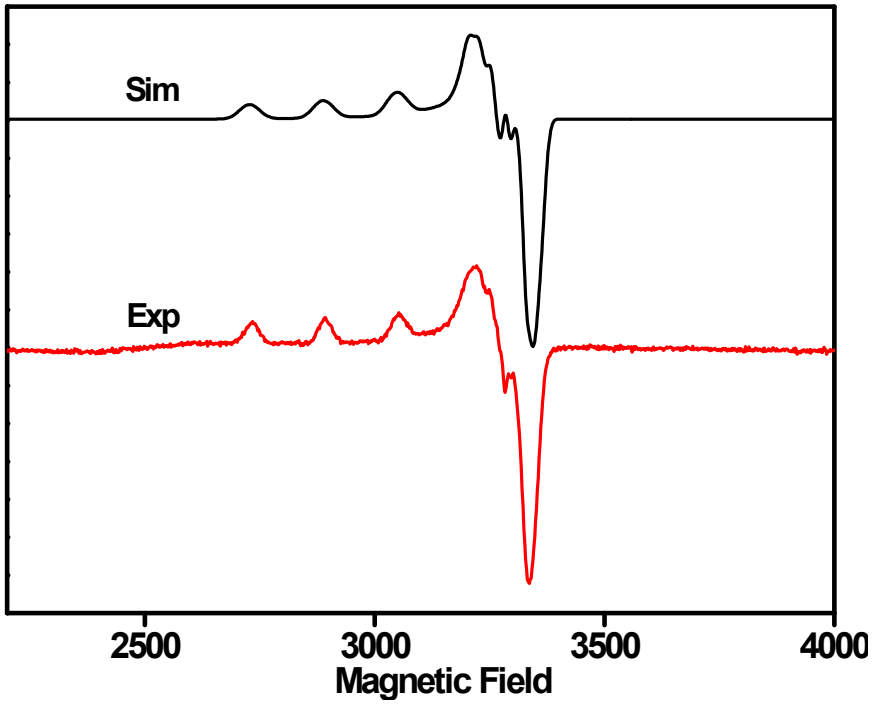

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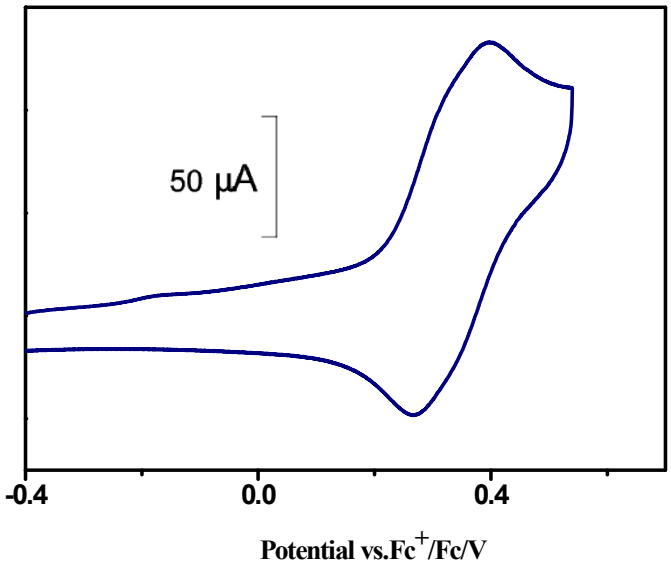

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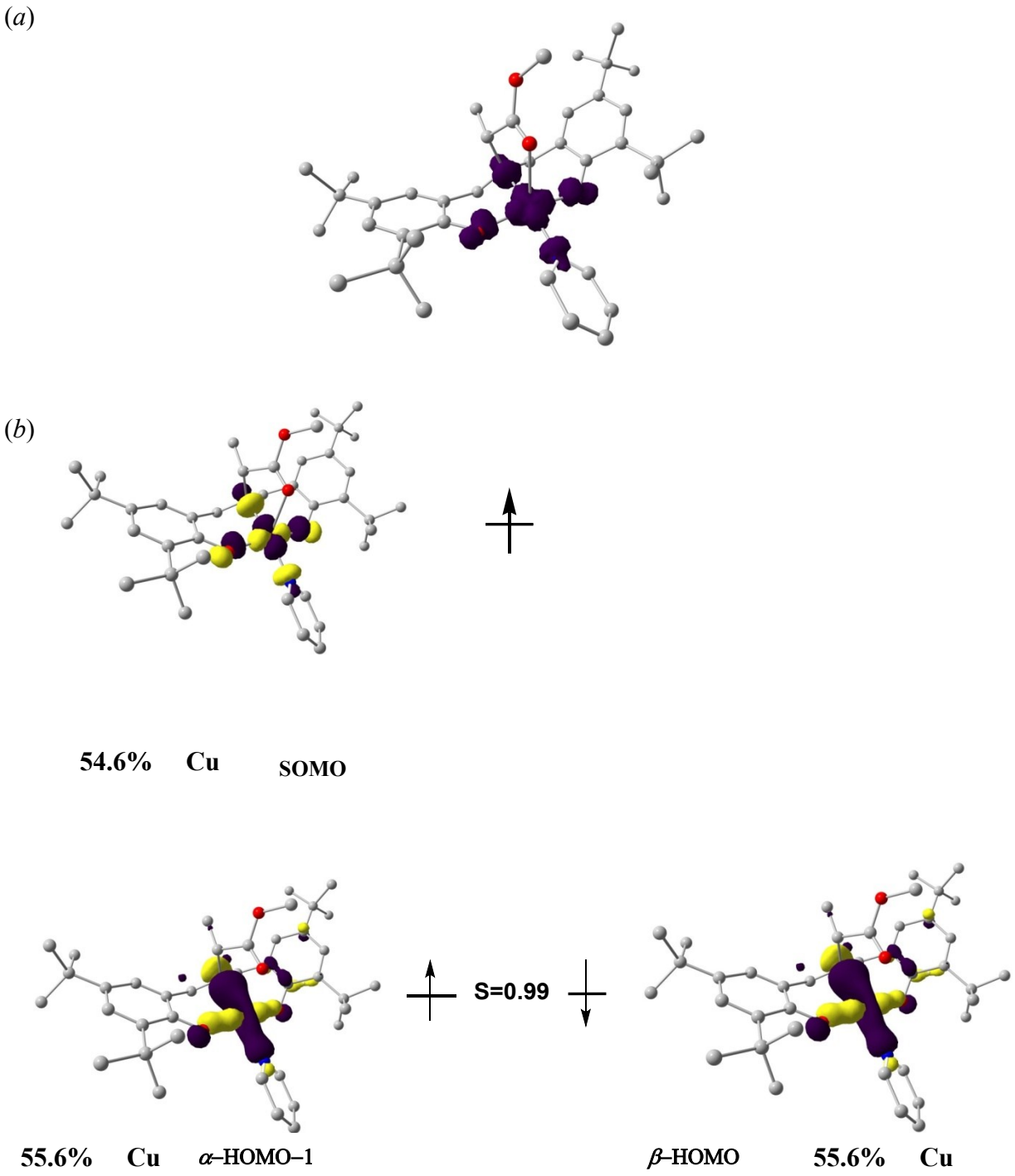


Fig. S8. *(a)* Spin-Density plot and *(b)* Magnetic orbitals for [^{1}LCu^{II}Py] (**4**) (M_s = ½).

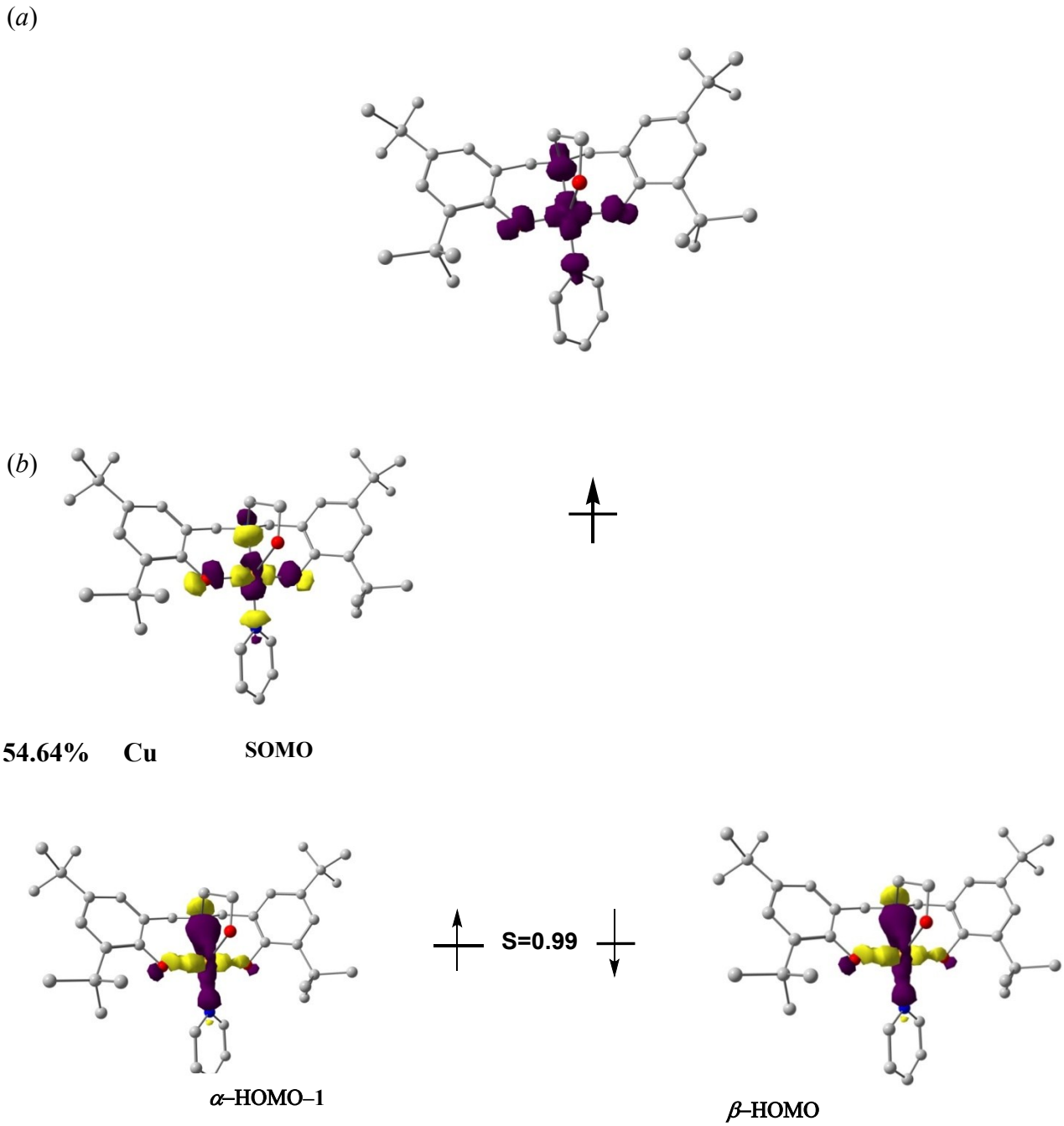


Fig. S9. *(a)* Spin-Density plot and *(b)* Magnetic orbitals for [^{2}LCu^{II}Py] (**5**) (M_s = ½).

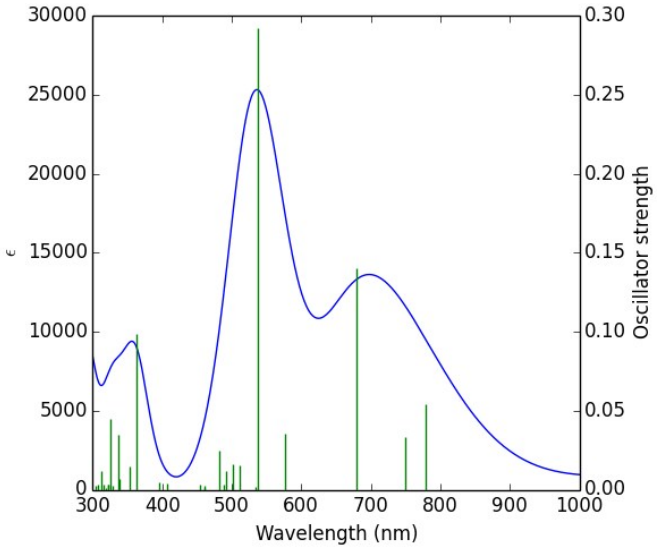
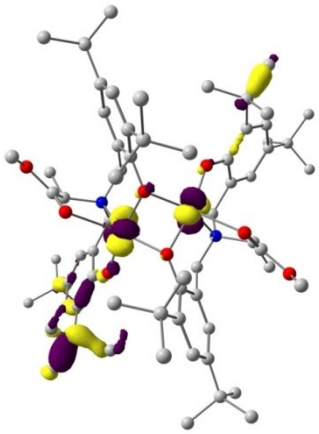
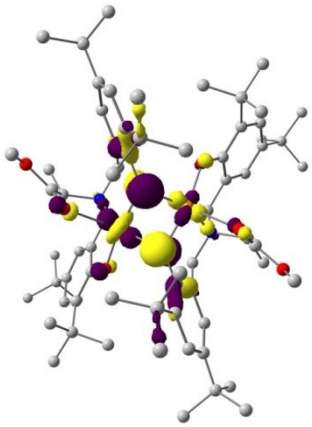


Fig. S10. TD-DFT calculated electronic spectra for [$^{1}L_2Cu^{II}_2$] (**1**).



Homo-19 (α/β)



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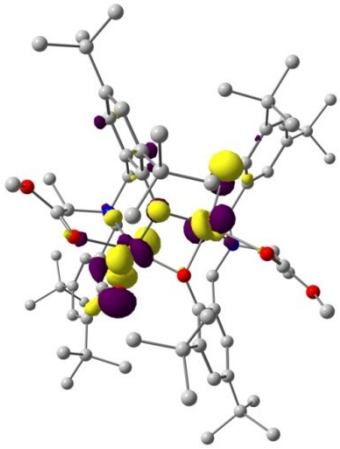

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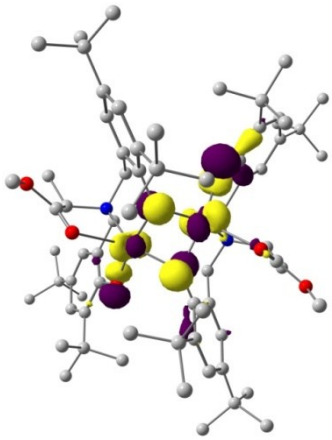
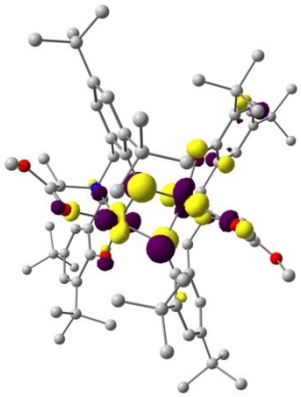


Homo-8 (α/β)



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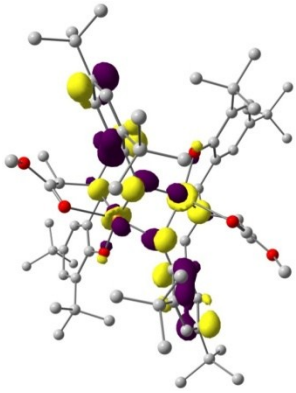

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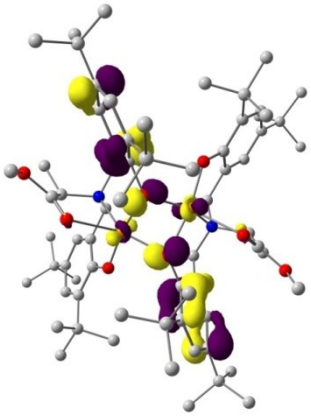

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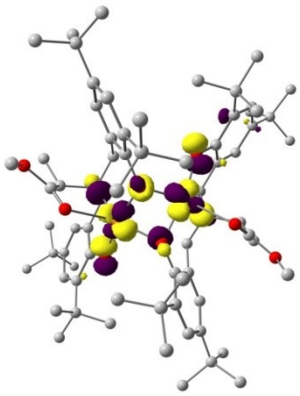
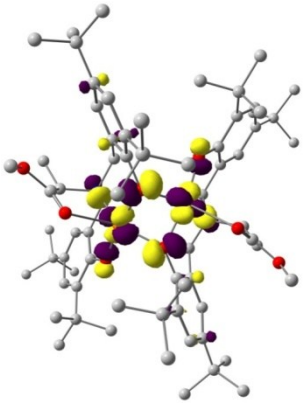


Homo (α/β)



Lumo (α/β)

Fig. S11. Representative molecular-orbitals involved in TD-DFT transitions of $[(^{1}L)_2Cu^{II}_2]$ (**1**).

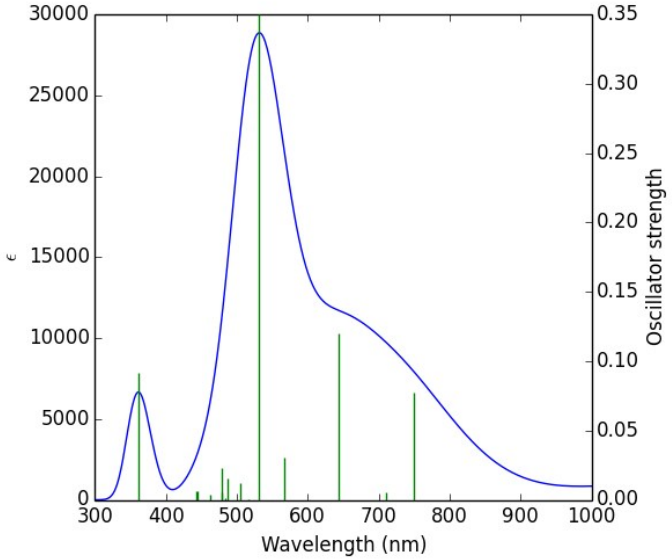
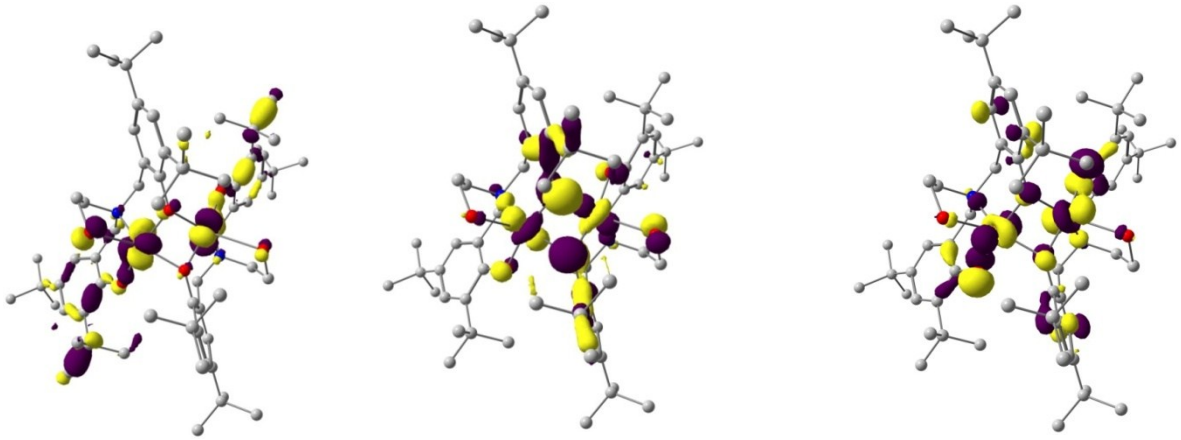
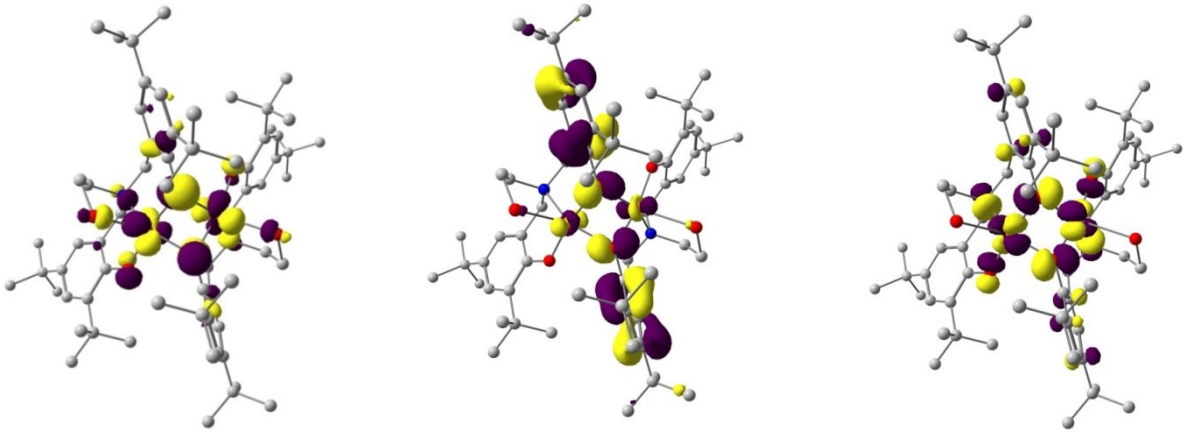


Fig. S12. TD-DFT calculated electronic spectra for $[(^2L)_2Cu^{II}_2]$ (**2**).



Homo-20 (α/β) **Homo-17 (α/β)** **Homo-11 (α/β)**



Homo-7 (α/β) **Homo-3 (α/β)** **LUMO (α/β)**

Fig. S13. Representative molecular-orbitals involved in TD-DFT transitions of [(^{2}L)$_2$Cu$^{II}_2$] (**2**)**.**

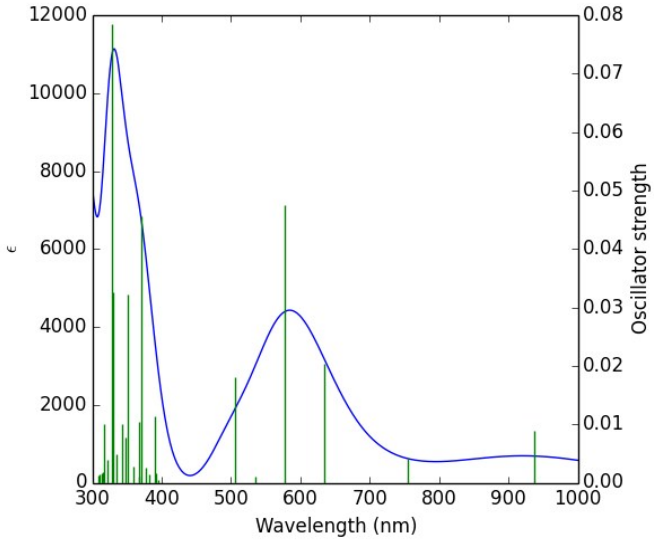
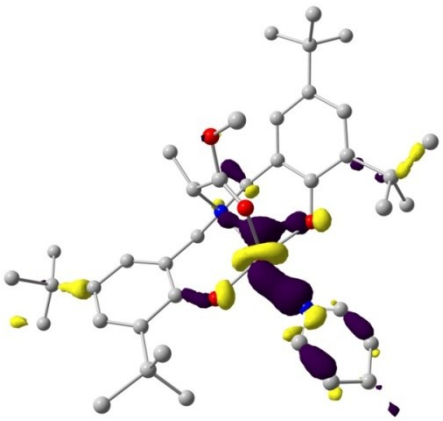
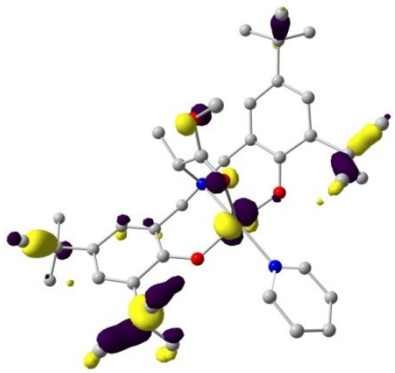


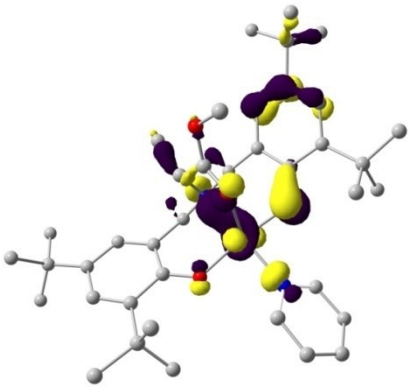
Fig. S14. TD-DFT calculated electronic spectra for [^{1}LCu^{II}Py] (**4**).



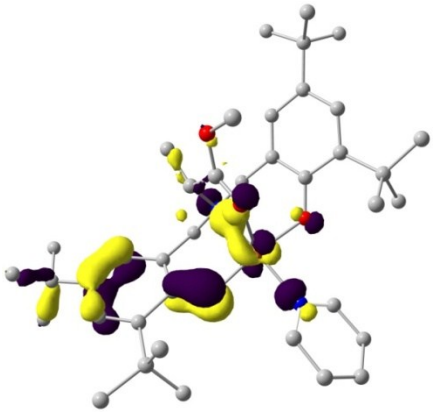
Homo-28 (β)



Homo-17 (β)



Homo-9 (β)



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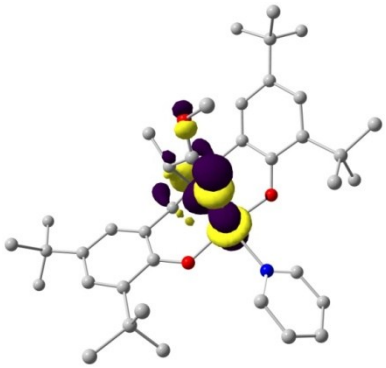

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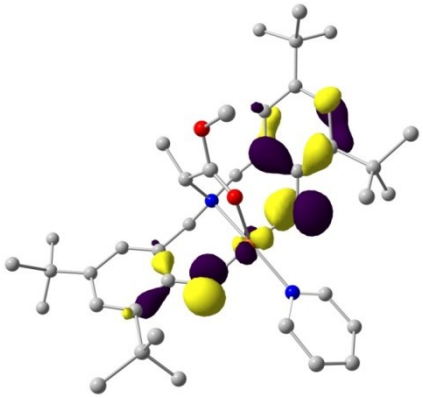

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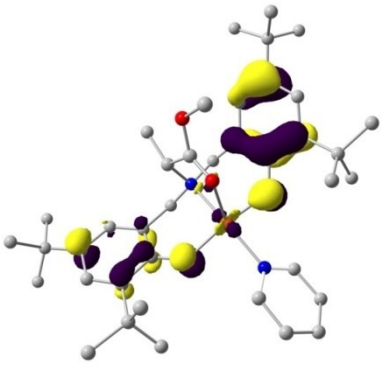

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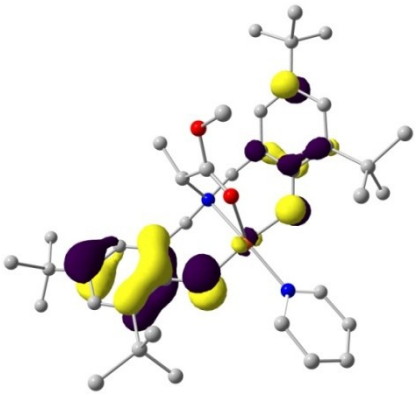

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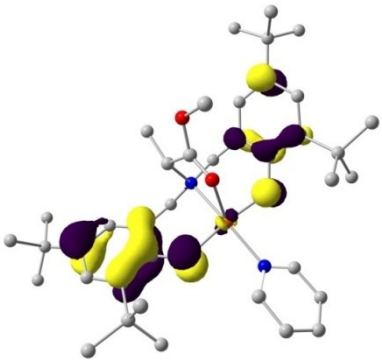
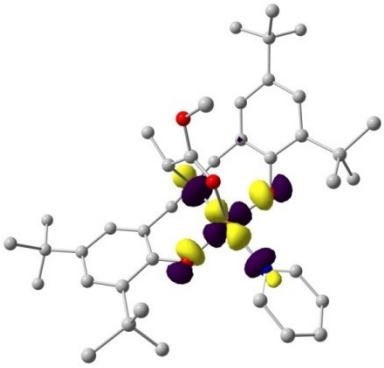
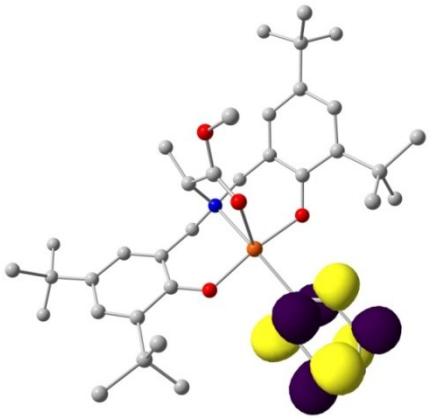


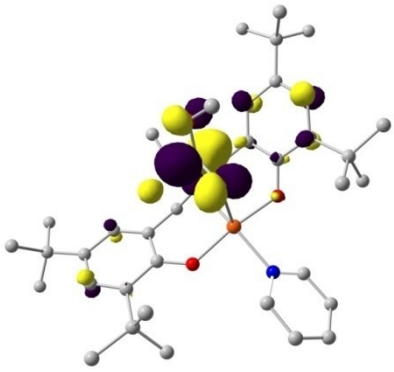
Homo (α)



Lumo (β)



Lumo+1 (α)



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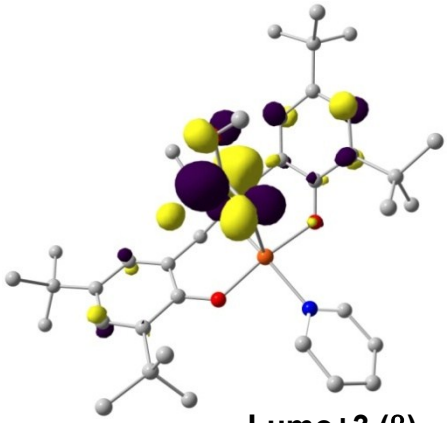


Lumo+3 (β)

Fig. S15. Representative molecular-orbitals involved in TD-DFT transitions of [^{1}LCu^{II}Py] (**4**).

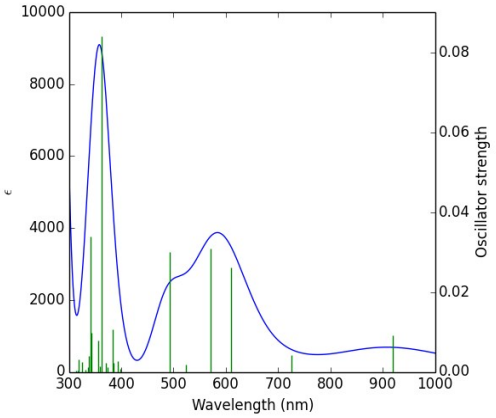
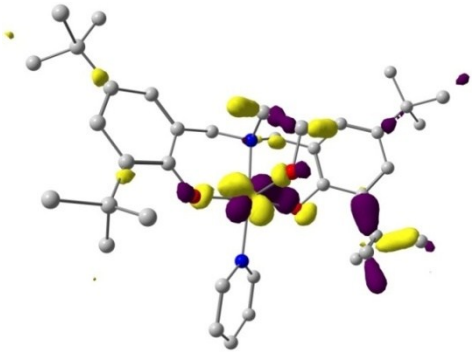
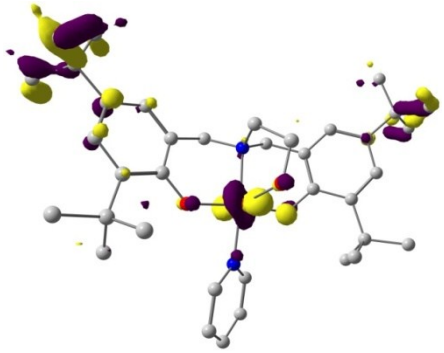


Fig. S16. TD-DFT calculated electronic spectra for [^{2}LCu^{II}Py] (**5**).



Homo-28 (β)



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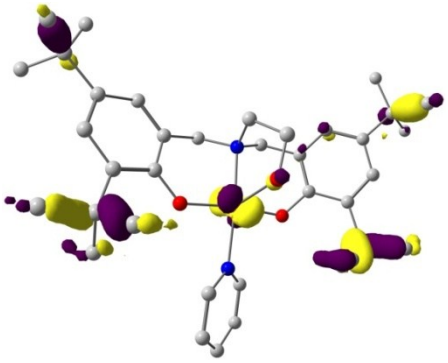

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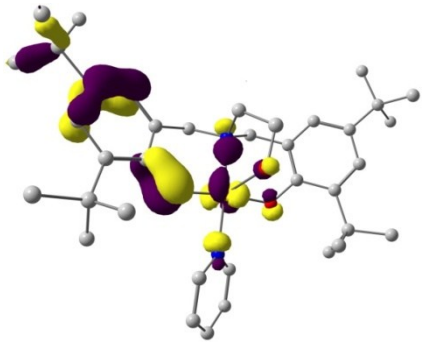

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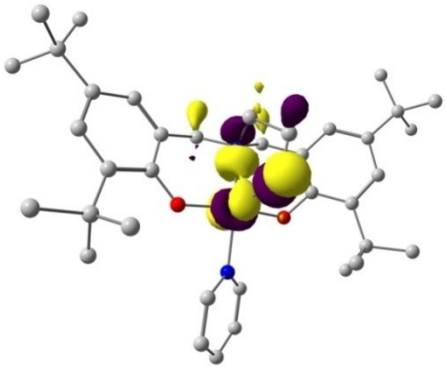
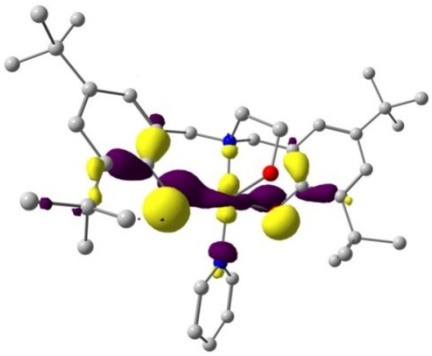
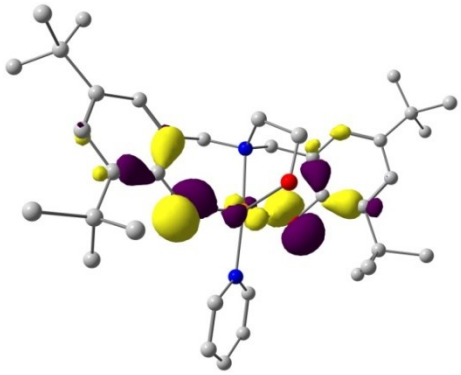


Homo-6 (β)



Homo-5 (β)



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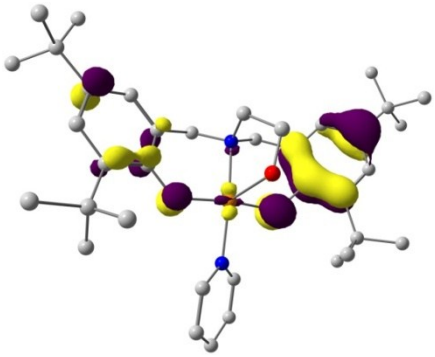

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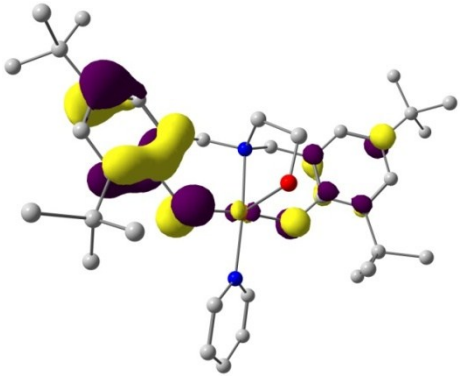
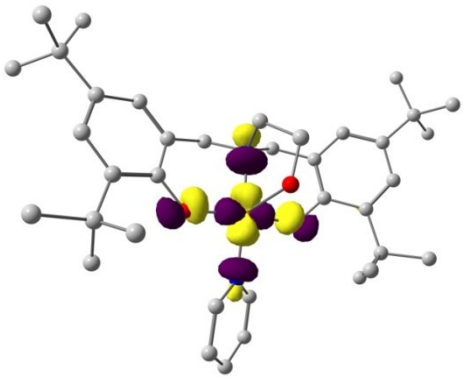


Homo (β)



LUMO (β)

Fig. S17. Representative molecular-orbitals involved in TD-DFT transitions of [^{2}LCu^{II}Py] (**5**).

Table S1 TD-DFT-calculated electronic transitions of $[(^{1}L)_2Cu^{II}_2]$ (**1**)

Excitation energy (eV)	λ (nm)	*F*	Transition	Character
1.5901	779	0.0543	*α/β*-H-8[~72%L]→*α/β* -L[~60%L] (14%)	Intra ligand Charge Transfer involving phenolate oxygen→ amine through Metal
			α/β-H-7[~59%L]→*α/β* -L[~60%L] (14%)	MLCT involving Metal → amine
			α/β-H-4[~87%L]→*α/β* -L[~60%L] (18%)	IntraligandChargetransferinvolving*tert*-butylphenolring→otherphenolateoxygenandamineandLMCTinvolving*tert*-butylphenolting → Metal
			α/β-H-3[~87%L]→*α/β* -L[~60%L] (37%)	LMCT involving one *tert*-butyl phenol ring→Metal and intra-ligand charge transfer involving one *tert*-butyl phenol ring→amine and other phenolate oxygen through metal
1.8266	678	0.1399	*α/β*-H-7[~59%L]→*α/β* -L[~60%L] (50%)	MLCT involving Metal → amine
			α/β-H-3[~87%L]→*α/β* -L[~60%L] (23%)	LMCT involving one *tert*-butyl phenol ring→ Metal and intra-ligand charge transfer involving one *tert*-butyl phenol ring→ amine and other phenolate oxygen through metal
			α/β-H[~59%L]→*α/β*-L[~60%L] (12%)	Intra ligand charge transfer between one bridged phenolate oxygen →other bridged
2.3053	537	0.2918	*α/β*-H-11[~60%L]→	MLCT involving Metal→ bridged

			α/β–L[~60%L] (57%)	phenolate oxygen
			α/β-H-3[~87%L]→*α/β* –L[~60%L] (23%)	LMCTinvolvingone*tert*-butylphenolring→Metalandintra-ligandchargetransferinvolvingone*tert*-butylphenolring→amineandotherphenolateoxygenthroughmetal
3.4105	363	0.0987	*α/β*-H-19[~62%L]→*α/β*–L[~60%L] (28%)	Intra-ligand charge transfer involving *tert*-butyl moieties→ phenolate oxygen, bridged phenolate oxygen and amine through Metal
			α/β-H-16[~78%L]→*α/β* -L[~60%L] (54%)	LMCT involving bridged phenolate oxygen→Metal and Intra-ligand charge transfer involving bridged phenolate → other phenolatemoieties

Table S2TD-DFT-calculatedelectronic transitions of [$^{2}L_2Cu_2^{II}$] (**2**)

Excitation energy (eV)	λ (nm)	*F*	Transition	Character
1.6553	789	0.0776	*α/β*-H-3[~87%L]→*α/β* -L[~60%L] (54%)	LMCT involving phenol→ Metal
1.9267	643	0.1199	*α/β*-H-7[~56%L]→*α/β* -L[~60%L] (62%)	LMCT involving phenolate → Metal
2.3310	531	0.3499	*α/β*-H-11[~64%L]→*α/β* –L[~60%L] (50%) *α/β*-H-	LMCT involving secondphenolate→ Metal LMCT involving phenol→ Metal
3.4293	361	0.0919	*α/β*-H-20[~56%L]→ *α/β*–L[~60%L] (28%) *α/β*-H-17[~74%L]→*α/β* –L[~60%L] (42%)	MLCT involving metal → phenolate Chargetransferinvolving*tert*-butyl → amine throughmetal Chargetransferinvolving alcohol→MetalandMLCT involving Metal →phenolate

Table S3 TD-DFT calculatedelectronic transitions of [^{1}LCu^{II}Py] (**4**)

Excitation energy (eV)	λ (nm)	*F*	Transition	Character
1.64	754	0.0042	*β*-H-6[~55%L]→ *β* -L[~51%L] (28%)	d-d transition
			β-H-1[~95%L]→ *β* -L[~51%L] (52%)	LMCT involving phenol→ Metal
1.95	634	0.0203	*β*-H-28[~58%L]→ *β* -L[~51%L] (15%)	LMCT involving pyridine → Metal
			β-H-6[~55%L]→ *β* -L[~51%L] (17%)	LMCT involving ester →Metal
			β-H-3[~93%L]→ *β* -L[~51%L] (26%)	LMCTinvolving phenol → Metal
2.14	577	0.0475	*β*-H-6[~55%L]→ *β* –L[~51%L] (21%)	LMCT involving ester →Metal
			β-H-1[~95%L]→ *β* –L[~51%L] (44%)	LMCT involving phenol→ Metal

2.44	506	0.018	*β*-H-17[~75%L]→ *β* –L[~51%L] (14%)	Intra ligand charge transfer involving*tert*-butyl →phenolate oxygen
			β-H-9[~81%L]→ *β* –L[~51%L] (13%)	Intra ligand charge transfer involvingphenol → phenolate oxygen
			β-H-8[~83%L]→ *β* –L[~51%L] (15%)	Intra ligand charge transfer involvingphenol → phenolate oxygen
			β-H[~98%L]→ *β* –L[~51%L] (18%)	LMCT involving phenol → Metal along with Intra ligand charge transfer involving phenol → pyridine
3.78	327	0.0784	*a*-H[~98%L]→ *a* –L+1[~93%L] (22%)	Intra ligand charge transfer involving phenol → pyridine
			a-H[~98%L]→ *a* –L+2[~100%L] (37%)	Intra ligand charge transfer involving phenol → ester
			β-H[~98%L]→ *β* –L+3[~100%L] (30%)	Intra ligand charge transfer involving phenol → ester

Table S4TD-DFT calculatedelectronic transitions of [^{2}LCu^{II}Py] (**5**)

Excitation energy (eV)	λ (nm)	*F*	Transition	Character
1.3497	918	0.0091	*β*-H[~97%L]→ *β* -L[~52%L] (74%)	Chargetransferinvolvingphenolate → pyridine and phenol→ amine andLMCT involving phenol→ Metal
1.7070	726	0.1199	*β*-H-6[~56%L]→ *β* -L[~52%L] (27%) *β*-H-1[~96%L]→ *β* -L[~52%L] (54%)	Chargetransferinvolving alcohol → phenolate Chargetransferinvolving phenol →pyridine andamine and LMCTinvolving phenol → Metal
2.0309	610	0.3499	*β*-H-28[~61%L]→ *β* –L[~52%L] (17%) *β*-H-6[~56%L]→ *β* –L[~52%L] (10%) *β*-H-4[~92%L]→ *β* –L[~52%L] (29%)	LMCT involving *tert*-butyl → Metal Chargetransferinvolving alcohol → phenolate Chargetransferinvolving phenol →pyridine andamine and LMCTinvolving phenolate →Metal

2.1712	571	0.0308	*β*-H-6[~56%L]→ *β* –L[~52%L] (23%) *β*-H-1[~96%L]→ *β* –L[~52%L] (41%)	Chargetransferinvolving alcohol → phenolate Chargetransferinvolving phenol →pyridine andamine and LMCTinvolving phenol → Metal
2.5176	492	0.0301	*β*-H-26[~72%L]→*β* –L[~52%L] (11%)*β*-H-17[~76%L]→ *β* –L[~52%L] (13%) *β*-H-8[~78%L]→ *β* –L[~52%L] (21%) *β*-H[~97%L]→ *β* –L[~52%L] (19%)	Chargetransferinvolving*tert*-butyl →pyridineandLMCT involving *tert*-butyl → Metal Chargetransferinvolving*tert*-butyl →amine , pyridine and LMCT involving*tert*-butyl →Metal LMCT involving phenol→ Metal Chargetransferinvolving phenol →amine and pyridine andLMCTinvolving phenol → Metal
3.4193	362	0.0836	*β*-H-28[~61%L]→ *β* –L[~52%L] (14%) *β*-H-5[~86%L]→ *β* –L[~52%L] (11%) *β*-H-4[~92%L]→ *β* –L[~52%L] (36%)	LMCT involving *tert*-butyl → Metal LMCT involving phenol→ Metal Chargetransferinvolvingphenolate → pyridine and LMCT involvingphenolate→ Metal
3.6273	341	0.0338	*β*-H-5[~86%L]→ *β* –L[~52%L] (48%)	LMCT involving phenol→ Metal

Table S5 DFT-optimizedCartesian coordinates of [(^{1}L)$_2$Cu$_2^{II}$](**1**).

C	0.231737000	-0.594205000	0.432011000
C	-0.009464000	-0.060909000	2.859791000
C	1.004286000	-0.187499000	1.708349000
C	2.006966000	-1.306287000	2.075325000
C	-4.011604000	10.760515000	2.317932000
C	1.762621000	1.130398000	1.456620000
C	-3.231751000	12.290296000	0.471972000
C	1.540293000	2.297596000	2.186078000
C	2.744932000	1.202479000	0.448803000
C	-2.997082000	11.864949000	1.940302000
C	2.827491000	6.754101000	-6.000409000
C	-3.265257000	13.086180000	2.838660000
C	-1.130923000	10.222322000	1.357937000
C	4.685007000	0.936381000	-1.635184000
C	0.806299000	9.794743000	-2.253853000
C	2.242031000	3.483346000	1.917766000
C	-1.561420000	11.325445000	2.101210000
C	3.490019000	2.344871000	0.142817000
C	4.971882000	5.486206000	-5.810534000
C	0.541265000	8.483760000	0.688094000
C	4.267928000	6.817944000	-5.460735000
C	1.920273000	4.717115000	2.712132000
C	1.981287000	7.383504000	-0.939558000
C	3.161561000	7.152442000	-3.146987000
C	3.223858000	3.542931000	0.891350000
C	4.234605000	3.345255000	-2.064016000
C	4.570927000	2.316910000	-0.959154000
C	0.160809000	9.699195000	1.484757000
C	4.995657000	7.982465000	-6.171987000
C	4.306923000	7.035046000	-3.935394000
C	1.684627000	9.882358000	-1.004510000
C	3.241241000	7.328466000	-1.758946000
C	-0.617359000	11.892499000	2.973722000
C	3.285015000	3.952537000	5.544377000
C	1.106169000	10.282855000	2.377329000
C	5.947117000	2.637890000	-0.330705000
C	2.612166000	6.527288000	4.187759000
C	0.695444000	11.427422000	3.136674000
C	3.873657000	4.348557000	4.189022000
C	5.541676000	7.125859000	-3.267011000
C	3.087539000	10.442367000	-1.225678000
C	4.494042000	7.373220000	-1.102742000
C	5.690406000	7.300441000	-1.885035000
C	4.523081000	11.656626000	-2.655550000
C	3.680591000	7.356324000	4.846329000

C	1.669918000	12.135277000	4.103000000
C	1.015466000	13.325616000	4.831740000
C	5.348431000	4.743307000	4.205213000
C	3.680553000	7.512081000	6.238829000
C	2.158814000	11.147250000	5.187285000
C	3.510982000	7.769888000	9.120754000
C	4.625153000	8.033118000	4.039560000
C	2.870900000	12.688198000	3.300908000
C	7.099767000	7.442989000	-1.264523000
C	7.360705000	6.330319000	-0.226674000
C	8.218399000	7.338639000	-2.321732000
C	4.620478000	8.316310000	6.884311000
C	7.225287000	8.833455000	-0.601618000
C	4.648297000	8.526686000	8.411071000
C	5.630374000	8.833415000	4.670574000
C	7.387613000	4.703937000	5.396908000
C	5.577701000	8.944093000	6.066217000
C	4.494742000	10.031838000	8.730944000
C	5.993082000	8.017954000	8.980652000
C	6.181334000	10.529404000	2.853105000
C	6.760631000	9.527491000	3.874994000
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H	2.742737000	-1.476934000	1.274620000
H	0.480606000	0.202452000	3.810573000
H	-3.898608000	9.867431000	1.683974000
H	-4.256126000	12.676132000	0.335445000
H	2.564252000	-1.050790000	2.990946000
H	-3.099377000	11.447603000	-0.224305000
H	-3.877211000	10.444750000	3.364822000
H	0.799026000	2.316834000	2.987485000
H	2.259457000	5.921730000	-5.556258000
H	2.941576000	0.298768000	-0.126312000
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H	-2.526574000	13.083192000	0.175096000
H	3.749564000	0.637432000	-2.134230000
H	2.273978000	7.687261000	-5.809638000

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H	2.170472000	7.089165000	-3.598751000
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H	4.468677000	4.635799000	-5.324168000
H	3.270893000	3.099500000	-2.540253000
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H	1.262699000	9.189552000	-3.046346000
H	1.142217000	4.481172000	3.459936000
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H	1.504135000	5.507696000	2.065862000
H	0.764147000	7.631268000	1.350592000
H	5.470471000	0.974358000	-2.406545000
H	2.002877000	6.576799000	-0.191150000
H	4.981569000	7.838301000	-7.265231000
H	2.220824000	3.695069000	5.438230000
H	5.010762000	3.328354000	-2.847263000
H	6.023186000	5.482017000	-5.484508000
H	4.172171000	4.363735000	-1.662361000
H	4.508949000	8.945782000	-5.949657000
H	1.233679000	10.634206000	-0.333369000
H	-0.919566000	12.757194000	3.558024000
H	1.886868000	6.184595000	4.944712000
H	2.057521000	7.155960000	3.474472000
H	3.875551000	3.446663000	3.551949000
H	6.048806000	8.059289000	-5.861365000
H	6.221274000	1.871400000	0.412950000
H	3.804450000	3.063406000	5.926286000
H	3.388036000	4.745781000	6.294584000
H	6.730599000	2.647035000	-1.107347000
H	5.940562000	3.615816000	0.165280000
H	6.444209000	7.056045000	-3.871121000
H	0.158757000	13.014655000	5.450542000
H	2.907778000	6.997009000	6.811018000
H	4.452680000	12.085659000	-3.661646000
H	0.671582000	14.107444000	4.136097000
H	1.309020000	10.782552000	5.787989000
H	2.519578000	8.104781000	8.777487000
H	3.578723000	6.681756000	8.963339000
H	5.322732000	10.905127000	-2.607595000
H	7.304979000	5.336954000	-0.695654000
H	2.533921000	13.442272000	2.570434000
H	2.667398000	10.281713000	4.746327000

H	4.714949000	12.440636000	-1.909553000
H	6.639142000	6.358266000	0.597501000
H	3.390128000	11.888989000	2.758656000
H	3.562527000	7.948943000	10.206408000
H	8.224708000	6.360954000	-2.828780000
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H	8.145812000	8.125011000	-3.089543000
H	2.862247000	11.650760000	5.871268000
H	6.463609000	8.985388000	0.170950000
H	7.116950000	9.632914000	-1.352613000
H	3.593730000	13.176060000	3.976805000
H	5.529179000	10.040757000	2.120509000
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H	3.541778000	10.422102000	8.340334000
H	6.124214000	6.942496000	8.779301000
H	7.919997000	4.163195000	4.601861000
H	9.194602000	7.456253000	-1.825791000
H	6.999461000	7.846365000	2.474392000
H	7.714524000	4.362877000	6.385883000
H	7.558040000	5.782845000	5.280936000
H	5.597954000	11.312620000	3.359286000
H	8.218071000	8.944748000	-0.135550000
H	4.512807000	10.199575000	9.820807000
H	6.034083000	8.167089000	10.072572000
H	6.329781000	9.558839000	6.556935000
H	6.998425000	11.018532000	2.298139000
H	5.306282000	10.629693000	8.289008000
H	6.851320000	8.548684000	8.540804000
H	8.085057000	7.780554000	3.882624000
H	8.408529000	8.933162000	2.566490000
H	7.201141000	11.136347000	5.325261000
H	8.217049000	9.683317000	5.530985000
H	8.502455000	10.785559000	4.171674000
N	1.764524000	8.650284000	-0.167523000
N	3.098140000	5.348575000	3.399046000
O	3.861700000	4.674917000	0.619637000
O	3.244373000	11.033085000	-2.411654000
O	2.321963000	9.766675000	2.513935000
O	4.522589000	7.515810000	0.236489000
O	3.946161000	10.433812000	-0.362510000
O	4.568700000	7.878071000	2.702821000
O	5.916188000	5.221183000	3.239726000
O	5.973611000	4.420470000	5.338928000
Cu	4.269338000	6.132007000	1.782271000
Cu	3.364710000	8.785114000	1.255128000

Table S6 DFT-optimizedCartesian coordinates of $[(^2L)_2Cu_2^{II}]$ (**2**)

Cu	0.095907000	0.020723000	-0.066698000
Cu	-0.031481000	0.019128000	2.754725000
O	1.769076000	0.187484000	-0.969255000
O	-1.427362000	-0.217076000	1.235329000
O	0.858080000	-1.204294000	1.451687000
N	-0.667310000	1.861143000	-0.760045000
C	2.088305000	1.044627000	-1.934427000
C	0.536590000	2.749812000	-0.902800000
H	1.018826000	2.755399000	0.089389000
C	-1.529497000	2.436918000	0.322183000
H	0.194724000	-2.676632000	-0.345215000
O	-1.086167000	1.262630000	3.758024000
N	1.813215000	0.752166000	3.483055000
C	-0.688012000	2.133707000	4.680854000
C	1.603486000	2.234054000	3.606847000
H	1.268954000	2.569526000	2.610516000
C	2.840445000	0.520926000	2.415920000
H	-2.062805000	-1.782198000	3.023484000
O	0.244538000	-1.371604000	4.716368000
C	-2.656723000	0.322804000	1.094818000
C	2.086739000	-1.740570000	1.619878000
C	-1.369859000	1.708599000	-2.060300000
C	3.042917000	0.701608000	-2.951845000
C	1.512021000	2.341905000	-1.969722000
H	0.191568000	3.781912000	-1.097820000
H	-0.895186000	2.510462000	1.219273000
H	-1.807557000	3.466681000	0.032300000
C	-2.773055000	1.656676000	0.640838000
C	0.616803000	-3.687090000	-0.399037000
C	-2.172460000	0.420787000	-2.211173000
C	2.184559000	0.141557000	4.787247000
C	-1.586302000	2.581469000	5.709561000
C	0.632017000	2.658103000	4.673407000
H	2.580733000	2.716363000	3.792263000
H	2.471235000	1.022541000	1.508178000
H	3.774281000	1.028599000	2.718754000

C	3.128025000	-0.921367000	2.113080000
C	-3.093843000	-2.153214000	3.043688000
C	1.647110000	-1.276680000	4.989880000
C	-3.847130000	-0.434988000	1.323590000
C	2.352227000	-3.122615000	1.371458000
H	-0.595325000	1.720318000	-2.838793000
H	-2.036020000	2.572894000	-2.242049000
C	3.694213000	-0.697332000	-2.999969000
C	3.362101000	1.674659000	-3.903846000
C	1.861292000	3.266659000	-2.964560000
C	-4.025873000	2.257355000	0.476017000
C	1.246388000	-4.114649000	0.944273000
H	1.366556000	-3.697287000	-1.203724000
H	-0.191421000	-4.383191000	-0.678770000
H	-2.508988000	0.356439000	-3.262275000
H	-3.060062000	0.412096000	-1.564309000
H	1.771165000	0.787200000	5.575419000
H	3.282816000	0.136864000	4.912360000
C	-3.027969000	2.035743000	5.805132000
C	-1.116817000	3.531144000	6.622456000
C	1.045273000	3.597728000	5.629685000
C	4.414329000	-1.432192000	2.318319000
C	-3.814401000	-1.935652000	1.695571000
H	-3.628589000	-1.638591000	3.855984000
H	-3.058707000	-3.227353000	3.288183000
H	1.866842000	-1.589462000	6.026580000
H	2.125720000	-1.994270000	4.313327000
C	-5.072519000	0.223795000	1.146959000
C	3.663152000	-3.571996000	1.583677000
C	4.459788000	-0.974316000	-1.685464000
C	2.593841000	-1.762590000	-3.212664000
C	4.702841000	-0.837792000	-4.157473000
H	4.091713000	1.414572000	-4.669230000
C	2.799075000	2.964973000	-3.951912000
H	1.378687000	4.245630000	-2.939902000
C	-5.208935000	1.562929000	0.739777000
H	-4.053647000	3.292289000	0.131724000
C	0.168569000	-4.175645000	2.051269000

C	1.785384000	-5.546746000	0.750072000
C	-3.809672000	2.373184000	4.514606000
C	-2.988311000	0.503815000	6.016243000
C	-3.808332000	2.640276000	6.989119000
H	-1.802768000	3.876239000	7.394641000
C	0.184560000	4.069191000	6.620837000
H	2.073297000	3.960446000	5.570754000
C	4.720186000	-2.767632000	2.045486000
H	5.180741000	-0.751892000	2.692780000
C	-3.093540000	-2.721715000	0.574984000
C	-5.227921000	-2.536993000	1.835416000
H	-5.984801000	-0.340598000	1.330276000
H	3.878320000	-4.620419000	1.387178000
H	4.926580000	-1.973039000	-1.719889000
H	3.793439000	-0.935321000	-0.815517000
H	5.263019000	-0.232390000	-1.542525000
H	3.033712000	-2.774430000	-3.210001000
H	2.093302000	-1.615281000	-4.183681000
H	1.834787000	-1.711478000	-2.423463000
H	5.130029000	-1.853123000	-4.144167000
H	5.540858000	-0.128245000	-4.068985000
H	4.232480000	-0.693786000	-5.142985000
C	3.220511000	3.955487000	-5.054992000
C	-6.609433000	2.187928000	0.586189000
H	0.604406000	-4.531582000	2.998802000
H	-0.632584000	-4.877559000	1.765813000
H	-0.282874000	-3.193568000	2.231904000
H	2.212100000	-5.962395000	1.676167000
H	2.551977000	-5.600472000	-0.038773000
H	0.956968000	-6.206573000	0.447804000
H	-4.835554000	1.972653000	4.573722000
H	-3.324818000	1.950052000	3.626654000
H	-3.881978000	3.465443000	4.383530000
H	-4.010695000	0.097874000	6.095692000
H	-2.459157000	0.253022000	6.951455000
H	-2.491773000	0.003505000	5.175485000
H	-4.823135000	2.212371000	7.011548000
H	-3.916404000	3.732775000	6.901440000

H	-3.336488000	2.418662000	7.959589000
C	0.592871000	5.117163000	7.674784000
C	6.125019000	-3.371023000	2.239050000
H	-3.621177000	-2.592180000	-0.386534000
H	-3.085934000	-3.799974000	0.802447000
H	-2.052157000	-2.394487000	0.469518000
H	-5.805999000	-2.471679000	0.900235000
H	-5.809651000	-2.051715000	2.634454000
H	-5.143184000	-3.603854000	2.095193000
C	2.908849000	3.354086000	-6.445131000
C	4.737819000	4.234766000	-4.949938000
C	2.478381000	5.299510000	-4.941037000
C	-6.539988000	3.662874000	0.150480000
C	-7.412899000	1.408185000	-0.480623000
C	-7.357616000	2.122233000	1.937955000
C	0.429478000	4.524893000	9.093666000
C	-0.307807000	6.366855000	7.537325000
C	2.056956000	5.563182000	7.509609000
C	7.138926000	-2.327140000	2.741635000
C	6.060551000	-4.517707000	3.274588000
C	6.639061000	-3.928555000	0.891166000
H	3.209521000	4.049396000	-7.246965000
H	1.830983000	3.153354000	-6.554498000
H	3.442367000	2.405688000	-6.610769000
H	5.060694000	4.938165000	-5.735968000
H	5.330570000	3.314214000	-5.062670000
H	4.989992000	4.675647000	-3.972246000
H	2.805258000	5.978591000	-5.744662000
H	2.681231000	5.801521000	-3.981833000
H	1.388039000	5.175625000	-5.037290000
H	-7.557778000	4.074127000	0.059328000
H	-6.048759000	3.780524000	-0.828327000
H	-5.997534000	4.281535000	0.882434000
H	-7.531930000	0.347850000	-0.210341000
H	-6.911621000	1.449571000	-1.461120000
H	-8.422078000	1.837370000	-0.596490000
H	-7.485288000	1.085977000	2.286297000
H	-8.362039000	2.568391000	1.846531000

H	-6.808920000	2.672055000	2.718727000
H	0.711696000	5.265741000	9.860565000
H	1.069867000	3.637973000	9.225664000
H	-0.609012000	4.219521000	9.293584000
H	-0.034814000	7.129159000	8.286412000
H	-1.370905000	6.121759000	7.683541000
H	-0.204265000	6.818442000	6.537748000
H	2.310189000	6.312704000	8.276289000
H	2.237277000	6.023562000	6.525446000
H	2.758160000	4.721719000	7.626769000
H	8.129040000	-2.794581000	2.862548000
H	6.850631000	-1.910350000	3.719734000
H	7.252661000	-1.491438000	2.033458000
H	5.380257000	-5.321640000	2.954501000
H	5.706261000	-4.148988000	4.250685000
H	7.058103000	-4.964581000	3.421016000
H	5.981208000	-4.717843000	0.496678000
H	7.645584000	-4.363063000	1.010874000
H	6.697527000	-3.132323000	0.132438000
O	-1.315576000	-0.688387000	-1.901806000
H	-1.864043000	-1.445043000	-1.644700000
H	-0.252952000	-0.847735000	5.366460000

Table S7 DFT-optmized Cartesiancoordinates of[$^{1}L_2Cu^{II}Py$] (**4**)

C	0.302917000	-0.330796000	-0.061297000
C	-0.240912000	0.270884000	2.299383000
C	0.915238000	0.044792000	1.308179000
C	1.766350000	-1.138048000	1.825828000
C	1.802079000	1.296315000	1.157244000
C	1.586892000	2.482204000	1.858510000
C	2.902470000	1.285400000	0.277562000
C	5.019645000	0.883524000	-1.611777000
C	2.414591000	3.603027000	1.693173000
C	3.769254000	2.362847000	0.074747000
C	2.088440000	4.866396000	2.436443000
C	3.525923000	3.577460000	0.807410000

C	4.794111000	3.322108000	-2.025841000
C	4.949888000	2.256590000	-0.914727000
C	3.119781000	3.938310000	5.334745000
C	6.283009000	2.446800000	-0.151439000
C	2.693175000	6.596168000	4.039757000
C	3.885000000	4.390392000	4.089957000
C	3.731753000	7.383917000	4.784872000
C	5.340835000	4.790756000	4.328544000
C	3.668777000	7.521221000	6.177849000
C	3.402638000	7.710391000	9.062057000
C	4.710601000	8.068939000	4.017394000
C	4.569397000	8.329518000	6.873849000
C	4.541730000	8.510584000	8.404553000
C	5.641538000	8.918613000	4.707019000
C	7.159680000	4.820479000	5.833120000
C	5.532820000	9.006928000	6.099073000
C	4.338349000	10.003945000	8.751826000
C	5.879562000	8.025727000	9.010231000
C	5.982240000	10.730997000	2.989771000
C	6.698806000	9.739237000	3.936883000
C	7.621322000	8.798416000	3.127640000
C	7.598946000	10.569792000	4.872705000
H	-0.332585000	-1.228024000	0.028706000
H	-0.853523000	-0.641596000	2.377229000
H	-0.318912000	0.490164000	-0.452604000
H	1.078773000	-0.547576000	-0.811514000
H	1.149359000	-2.046241000	1.933165000
H	-0.904869000	1.088060000	1.975814000
H	2.593578000	-1.376547000	1.139793000
H	0.125146000	0.509186000	3.310680000
H	2.205302000	-0.905942000	2.809480000
H	0.750923000	2.569040000	2.555385000
H	3.091078000	0.368681000	-0.279925000
H	4.115789000	0.672510000	-2.204625000
H	3.886580000	3.124985000	-2.619407000
H	5.162205000	0.057843000	-0.896939000

H	1.214838000	4.691815000	3.089374000
H	1.806497000	5.673949000	1.738913000
H	5.877014000	0.869419000	-2.303879000
H	2.082816000	3.681083000	5.073230000
H	5.656989000	3.292282000	-2.713529000
H	4.710813000	4.331520000	-1.605234000
H	1.907724000	6.246870000	4.731314000
H	2.205514000	7.245480000	3.295157000
H	3.974661000	3.520768000	3.417634000
H	6.446652000	1.612321000	0.549709000
H	3.590264000	3.036677000	5.749992000
H	3.112166000	4.700264000	6.123494000
H	7.133962000	2.464603000	-0.853981000
H	6.284704000	3.376445000	0.431709000
H	2.877738000	6.989745000	6.710104000
H	2.413824000	8.029536000	8.696577000
H	3.501307000	6.628665000	8.879557000
H	3.416809000	7.863915000	10.153010000
H	5.317900000	10.203531000	2.294271000
H	3.387568000	10.377408000	8.339295000
H	6.042978000	6.957149000	8.795765000
H	7.824884000	4.270965000	5.151961000
H	7.047216000	8.168549000	2.438345000
H	7.329429000	4.514164000	6.871855000
H	7.326304000	5.900047000	5.714399000
H	5.373737000	11.446691000	3.566151000
H	4.317694000	10.150214000	9.844958000
H	5.884202000	8.157118000	10.105449000
H	6.238483000	9.649053000	6.624800000
H	6.719108000	11.307477000	2.404487000
H	5.146382000	10.632588000	8.347694000
H	6.737595000	8.583561000	8.604660000
H	8.187051000	8.135593000	3.802308000
H	8.350573000	9.386128000	2.544326000
H	7.027702000	11.306156000	5.459687000
H	8.164784000	9.936489000	5.574243000

H	8.332468000	11.129569000	4.270689000
N	3.215518000	5.432260000	3.254540000
O	4.306183000	4.637412000	0.658712000
O	4.718134000	7.930602000	2.699290000
O	6.052905000	5.245665000	3.452556000
O	5.780626000	4.501735000	5.556810000
Cu	4.551981000	6.202043000	1.796781000
C	5.358132000	8.376895000	-0.109281000
C	6.433228000	6.380247000	-0.555981000
C	5.984868000	9.007386000	-1.183407000
H	4.670298000	8.905605000	0.551186000
C	7.118052000	6.938900000	-1.635194000
H	6.559401000	5.335511000	-0.276329000
C	6.886522000	8.276536000	-1.959553000
H	5.769699000	10.056202000	-1.395942000
H	7.814646000	6.325287000	-2.209183000
H	7.401239000	8.742697000	-2.803462000
N	5.574961000	7.087872000	0.192042000

Table S8 DFT-optmized Cartesian coordinates of [$^{2}L_{2}Cu^{II}Py$] (**5**)

Cu	0.041552000	-0.087596000	-0.048478000
O	0.033202000	-0.139601000	1.892307000
O	0.313674000	-0.126051000	-1.992691000
N	-1.917872000	-0.803374000	-0.189027000
C	-0.932997000	-0.490214000	2.730398000
C	-2.031521000	-1.838294000	0.896050000
H	-1.195799000	-2.538625000	0.722958000
C	-2.063299000	-1.514903000	-1.498678000
H	2.106987000	-0.039214000	-3.574496000
C	-0.642980000	-0.002006000	-2.905585000
C	-2.904731000	0.289201000	0.008242000
C	-0.921963000	-0.058727000	4.102363000
C	-2.007137000	-1.314666000	2.304154000
H	-2.965641000	-2.408038000	0.738474000
H	-1.308389000	-2.318384000	-1.480593000
H	-3.057709000	-1.997936000	-1.523280000

C	-1.881199000	-0.671705000	-2.727175000
C	-2.571857000	1.607351000	-0.686106000
C	2.013956000	0.580811000	-4.473999000
C	-0.472883000	0.798965000	-4.084806000
H	-2.957104000	0.471474000	1.090036000
H	-3.910050000	-0.041176000	-0.317170000
C	0.206625000	0.845978000	4.641272000
C	-1.959741000	-0.485608000	4.935554000
C	-3.027982000	-1.695967000	3.187132000
C	-2.904118000	-0.582197000	-3.677844000
H	-3.304923000	2.358229000	-0.337692000
H	-2.660520000	1.524237000	-1.776716000
C	0.837679000	1.575824000	-4.341836000
H	1.860072000	-0.085955000	-5.337647000
H	2.963319000	1.121483000	-4.628314000
C	-1.530577000	0.847720000	-5.001600000
C	1.568109000	0.125365000	4.492717000
C	0.203094000	2.187918000	3.869588000
C	0.036200000	1.183885000	6.135746000
H	-1.944114000	-0.161112000	5.975197000
C	-3.031496000	-1.301827000	4.525084000
H	-3.827530000	-2.327788000	2.794854000
C	-2.756591000	0.173302000	-4.844385000
H	-3.829961000	-1.126982000	-3.483268000
C	1.106011000	2.560240000	-3.178000000
C	0.788380000	2.406145000	-5.639660000
H	-1.398881000	1.449617000	-5.899632000
H	2.390997000	0.782094000	4.824602000
H	1.752446000	-0.177033000	3.454738000
H	1.591209000	-0.781635000	5.118588000
H	1.067219000	2.808630000	4.163382000
H	-0.711051000	2.759539000	4.097623000
H	0.229594000	2.030400000	2.783837000
H	0.866224000	1.832434000	6.459555000
H	0.055887000	0.284394000	6.771028000
H	-0.900927000	1.726303000	6.336996000

C	-4.123138000	-1.713262000	5.532260000
C	-3.848698000	0.285142000	-5.926756000
H	0.291255000	3.301975000	-3.104145000
H	2.040536000	3.119915000	-3.350409000
H	1.199176000	2.027125000	-2.222905000
H	-0.014236000	3.160418000	-5.622182000
H	0.646814000	1.776030000	-6.531437000
H	1.741964000	2.943116000	-5.766594000
C	-4.806978000	-0.452855000	6.110824000
C	-3.486519000	-2.521167000	6.687075000
C	-5.210219000	-2.588142000	4.881632000
C	-5.112359000	-0.513133000	-5.557687000
C	-4.254407000	1.765916000	-6.111916000
C	-3.308030000	-0.265616000	-7.267099000
H	-5.587924000	-0.732383000	6.838138000
H	-5.280795000	0.139945000	5.312085000
H	-4.089213000	0.200791000	6.629651000
H	-4.252123000	-2.821207000	7.422537000
H	-2.722239000	-1.936370000	7.221723000
H	-3.001221000	-3.434130000	6.306686000
H	-5.971917000	-2.859548000	5.630006000
H	-4.795776000	-3.525194000	4.477537000
H	-5.725172000	-2.061806000	4.062227000
H	-5.867333000	-0.410668000	-6.353403000
H	-5.567652000	-0.151721000	-4.622013000
H	-4.899324000	-1.587324000	-5.441077000
H	-3.399958000	2.390392000	-6.414569000
H	-4.658252000	2.183716000	-5.175613000
H	-5.029706000	1.863581000	-6.890372000
H	-2.422323000	0.291027000	-7.609415000
H	-4.074549000	-0.192011000	-8.056907000
H	-3.019074000	-1.324214000	-7.169275000
O	-1.246589000	2.023554000	-0.322719000
H	-0.834002000	2.438347000	-1.094946000
C	2.938260000	-0.394733000	-0.780602000
C	2.649776000	1.023581000	1.021656000

C	4.325234000	-0.265314000	-0.719164000
H	2.444939000	-1.004654000	-1.538406000
C	4.025165000	1.224134000	1.140543000
H	1.940878000	1.493138000	1.701802000
C	4.880783000	0.563903000	0.257325000
H	4.951484000	-0.804366000	-1.432417000
H	4.409384000	1.883306000	1.921015000
H	5.963660000	0.693078000	0.328721000
N	2.119537000	0.234596000	0.076106000