Electronic Supplementary Material (ESI) for Dalton Transactions

Peculiar properties of homoleptic Cu complexes with dipyrromethene derivatives.

Supplementary Information

Figures

Mass spectrometry

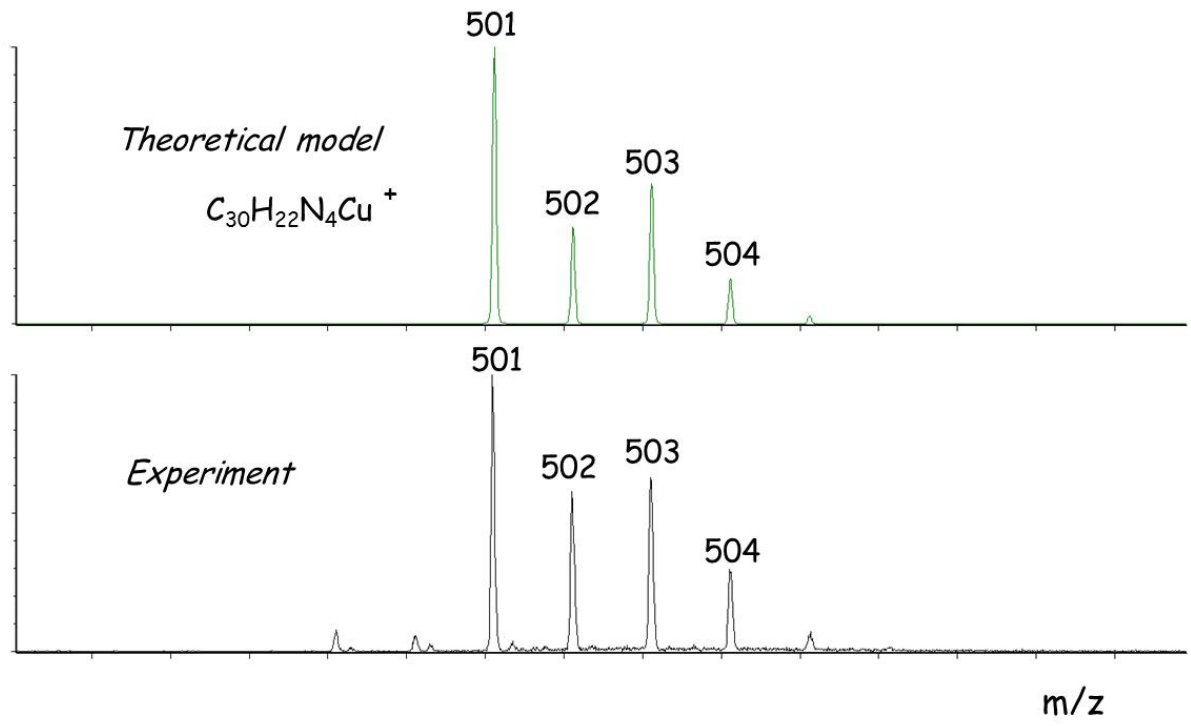


Figure S1: MALDI(+) mass spectrometry analysis of the $[Cu(II)(dipy)_2]$ complex: comparison between the experimental data and the theoretical isotope model for the $[Cu(II)(dipy)_2]^+$ cations.

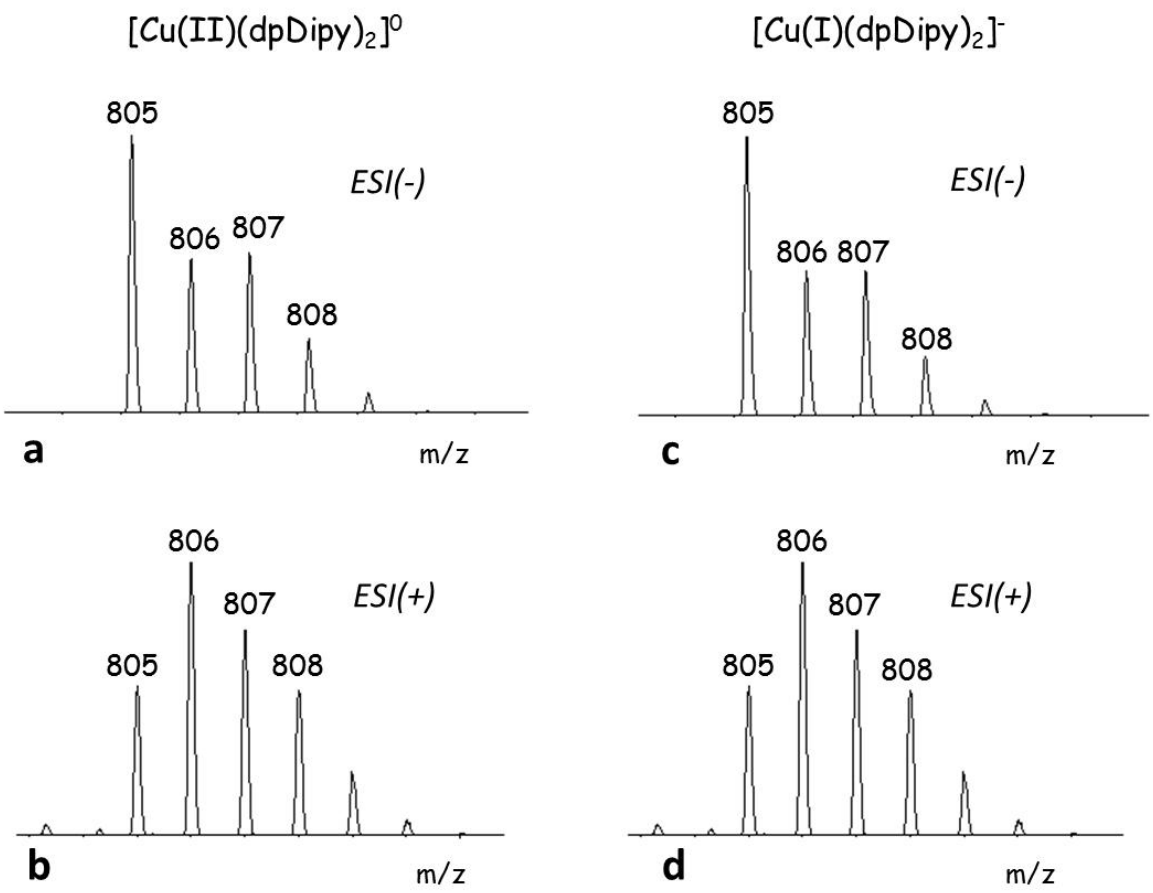


Figure S2 : ESI mass spectrometry analyses of the Cu(II) and presumed Cu(I) complexes with dpDipy as ligand: (**a**) ESI(-) and (**b**) ESI(+) analyses of $[Cu(II)(dpdipy)_2]$ and (**c**) ESI(-) and (**d**) ESI(+) analyses of the crude presumed $[Cu(I)(dpdipy)_2]^-$.

XR structures

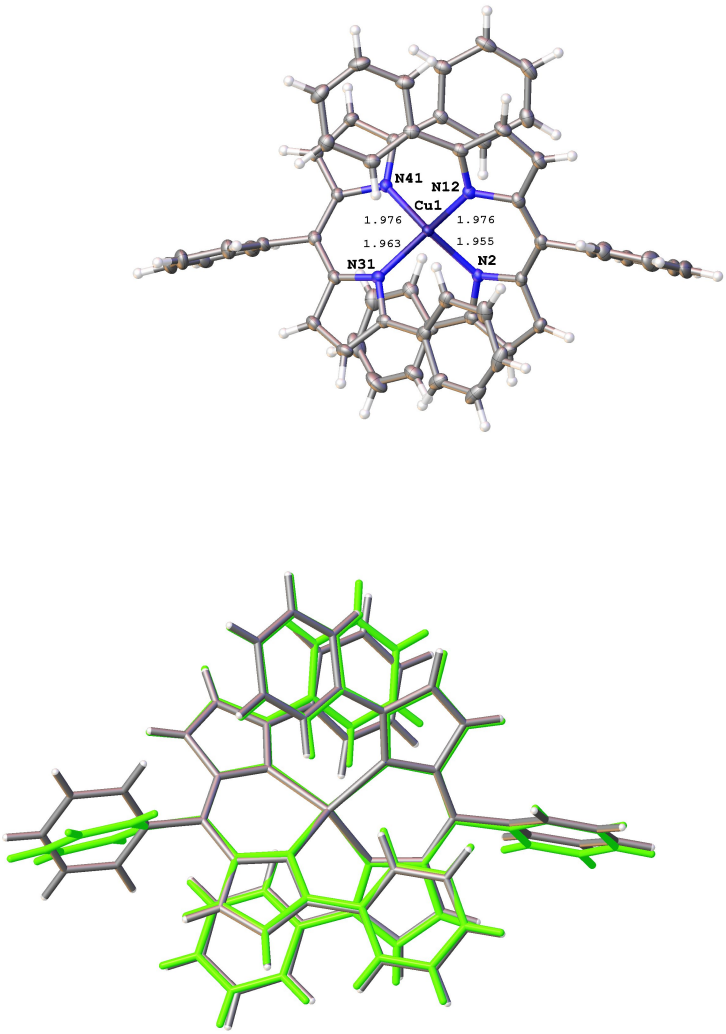


Figure S3: XR structure of the big crystals obtained for the last trial of synthesis of $[Cu(I)(dpDipy)_2]^-$ (above) and for the superposition of this latter (in green) to $[Cu(II)(dpDipy)_2]$ (below) for comparison.

EPR data

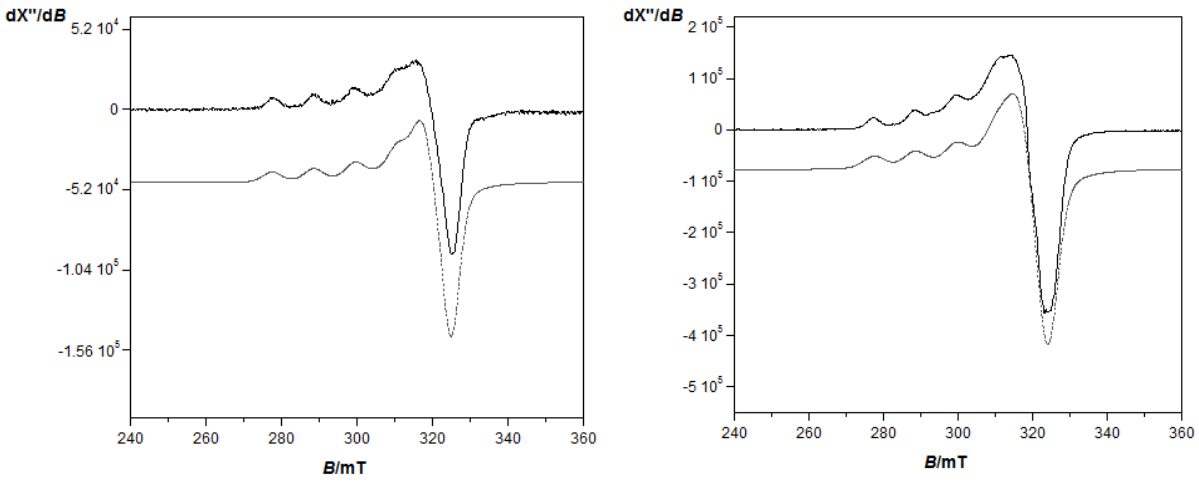
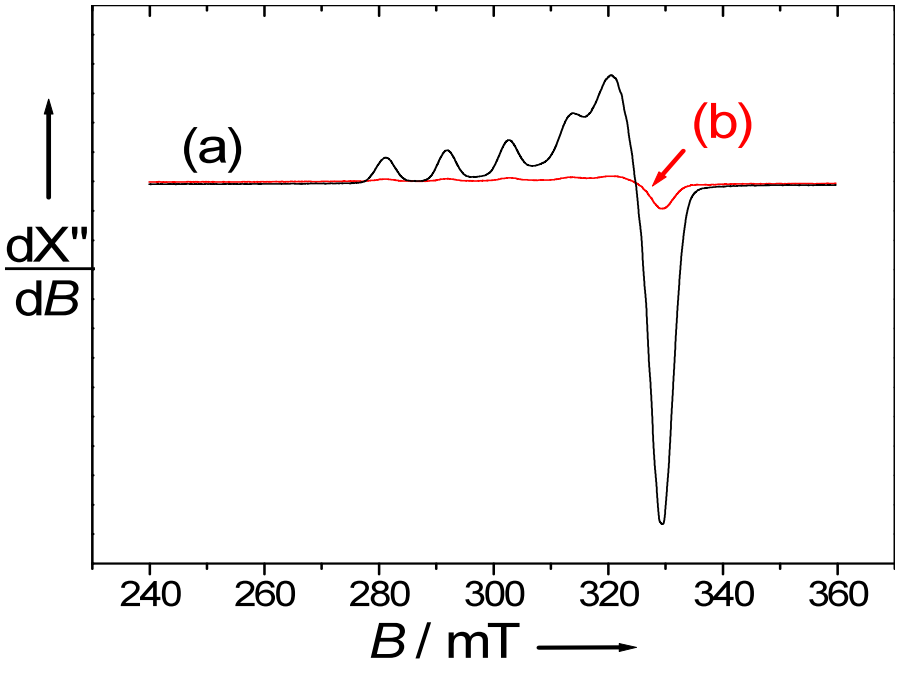


Figure S4: (a) RPE spectrum of the small crystals obtained for the last trial of synthesis of $[Cu(I)(dpdipy)_2]^-$, recorded in benzonitrile at 100 K. Micro-wave frequency = 9.33 GHz, power = 20 mW, amplitude of modulation 0.2 mT, modulation frequency = 100 KHz. (b) RPE spectrum of $[Cu(II)(dpdipy)_2]$ recorded in the same experimental conditions Dotted line: simulated spectrum.



(c)

Figure S4c: EPR spectra of $[Cu^{II}(dpdipy)_2]$ in 1 mM benzonitrile solution (+0.1 M $TBAPF_6$): (a) Before electrolysis; (b) After electrolysis at -0.59 V/SCE in the glove box. Microwave Freq: 9.34 GHz, power: 5 mW, Mod. Amp: 0.4 mT, Freq: 100 KHz, T = 100 K.

Electrochemical data

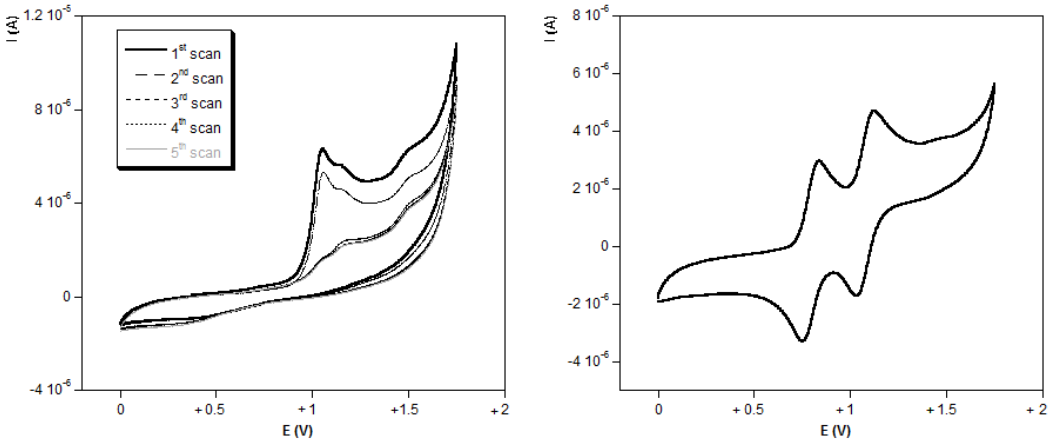


Figure S5: Oxidation voltamograms of [Cu(II)(dipy)$_2$] (left) and [Cu(II)(dpdipy)$_2$] (right) in PhCN.

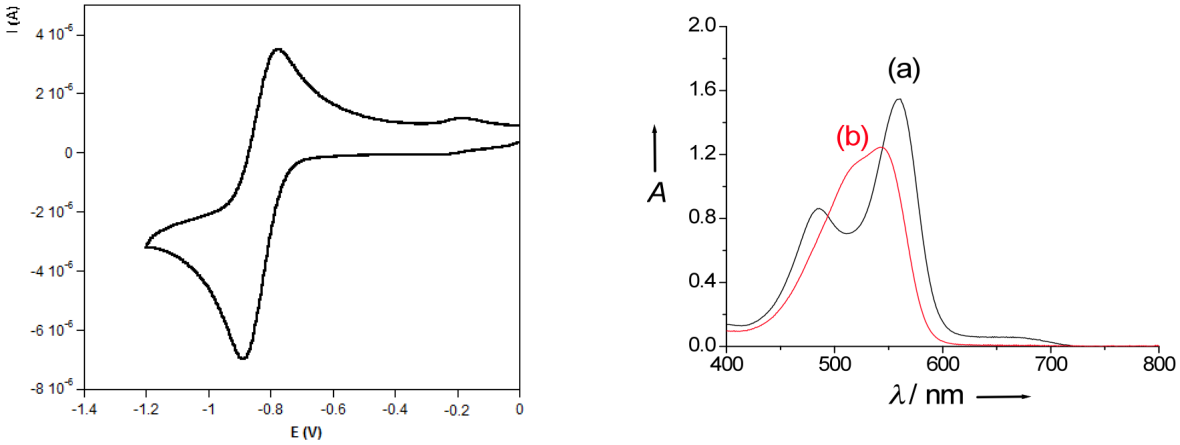


Figure S6: (Left, a) Reduction voltammogram of [Cu(II)(dipy)$_2$] in PhCN.(Right, b) Absorption spectra of [Cu^{II}(dpdipy)$_2$] 0.02 mM in benzonitrile solution (+0.1 M TBAPF$_6$). T = 298 K, l = 1.000 cm. (a) Before electrolysis; (b) After electrolysis at -0.59 V/SCE in the glove box.

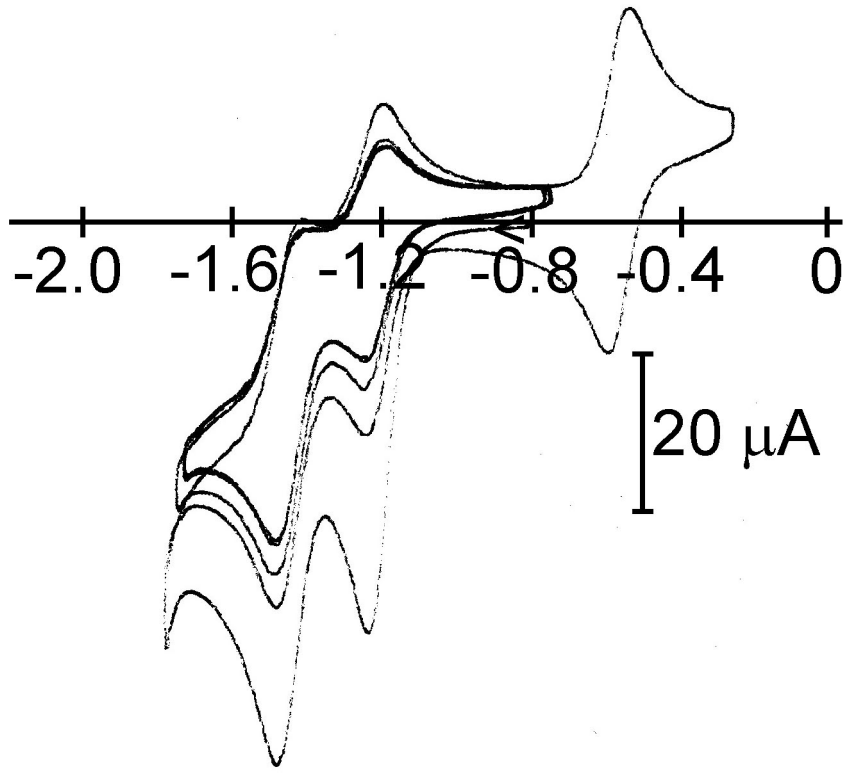
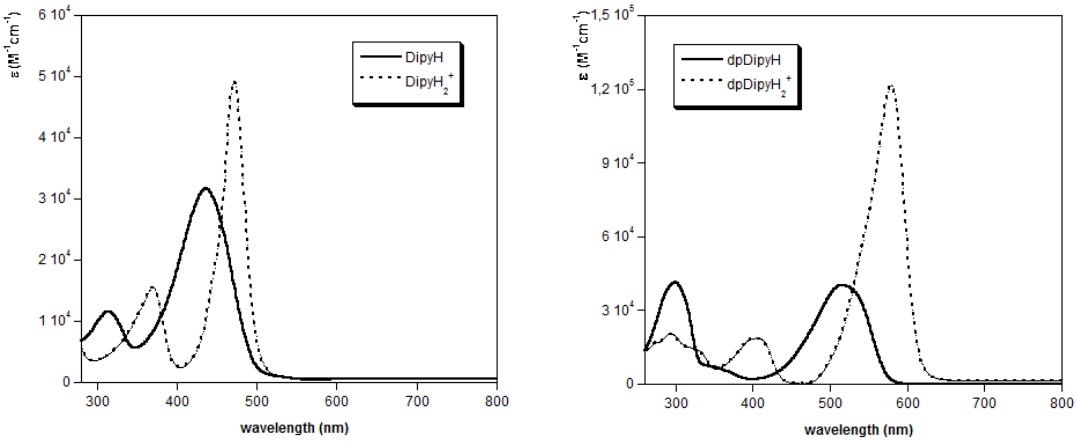


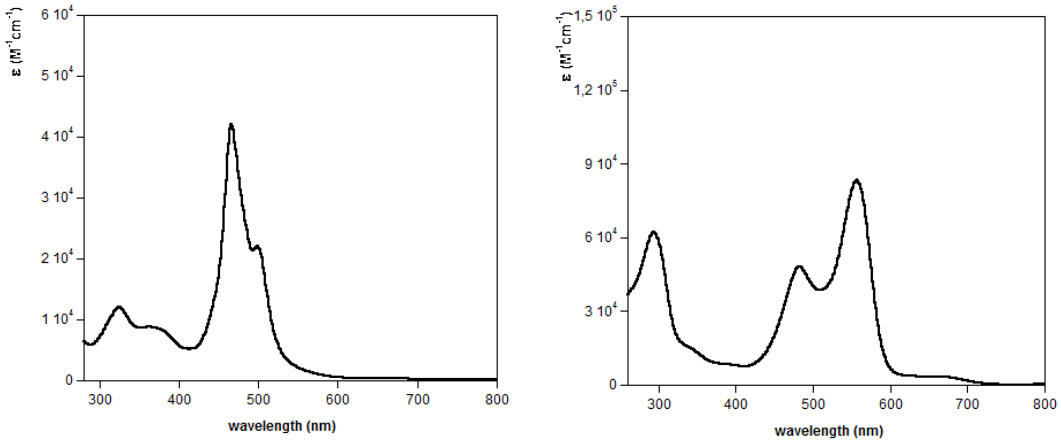
Figure S7: CV curve of $[Cu^{II}(dpdipy)_2]$ after one-electron electrochemical reduction in 1 mM benzonitrile solution (+0.1 M $TBAPF_6$) at a platinum disc, recorded in the glove box. Scan rate = 0.1 V / s; T = 298 K. The potential values are converted against the SCE electrode.

Spectroscopy: Absorption, emission.



A B

Figure S8: UV/Vis absorption spectra for (A) dipyH (solid line - TEA) and $dipyH_2^+$ (dotted line – TFA) ; (B) dpdipyH (solid line - TEA) and $dpdipyH_2^+$ (dotted line – TFA) recorded in $CHCl_3$.



A B

Figure S9. UV/Vis absorption spectra for (A) $[Cu(II)(dipy)_2]$ and (B) $[Cu(II)(dpdipy)_2]$ recorded in $CHCl_3$.

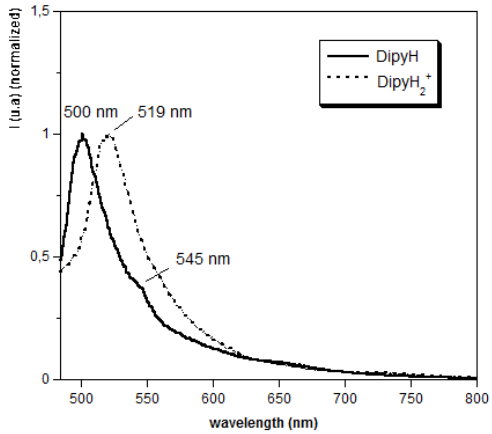


Figure S10: Emission spectra of dipyH (non protonated, 2.7 10^{-6} M) and $dipyH_2^+$ (protonated, 2.8 10^{-6} M) in $CHCl_3$. $\lambda_{excitation}$ = 465 nm.

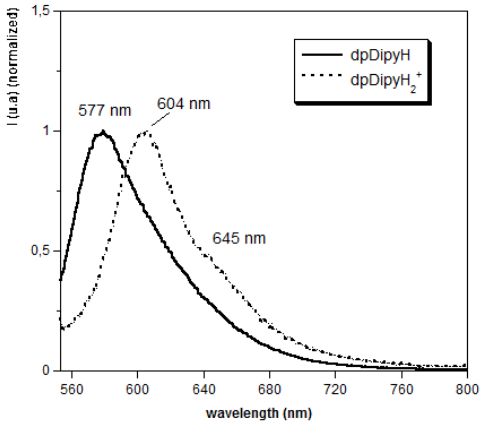


Figure S11: Emission spectra of dpdipyH (non protonated, 3.5 10^{-6} M) and $dpdipyH_2^+$ (protonated, 1.4 10^{-6} M) in $CHCl_3$. $\lambda_{excitation}$ = 530 nm.

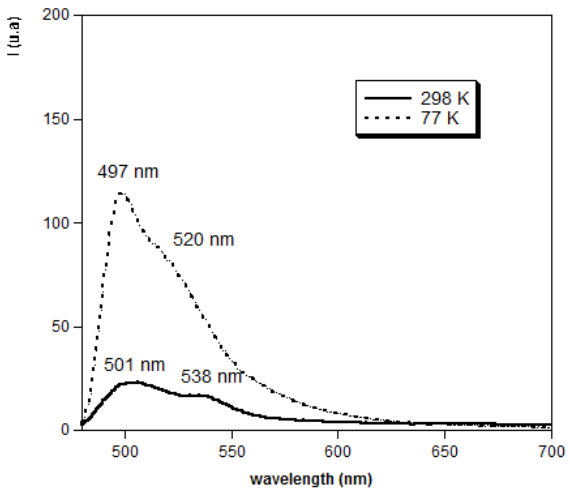


Figure S12: Emission spectra of [Cu(II)(dipy)$_2$] at 298K and 77K in the mixture EtOH/MeOH (4/1)(4.7 10^{-6} M).

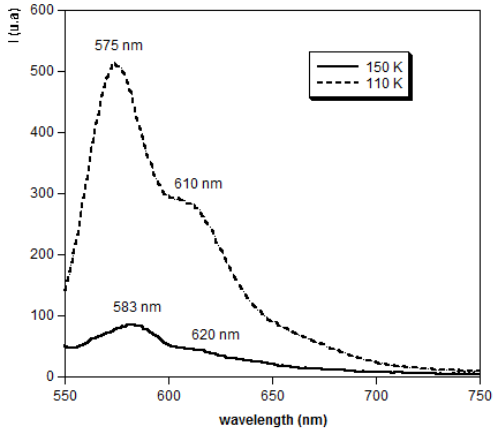


Figure S13: Emission spectra of [Cu(II)(dpdipy)$_2$] at 150K and 110K in butyronitrile (2.5 10^{-6}M).$\lambda_{excitation}$ = 540 nm.

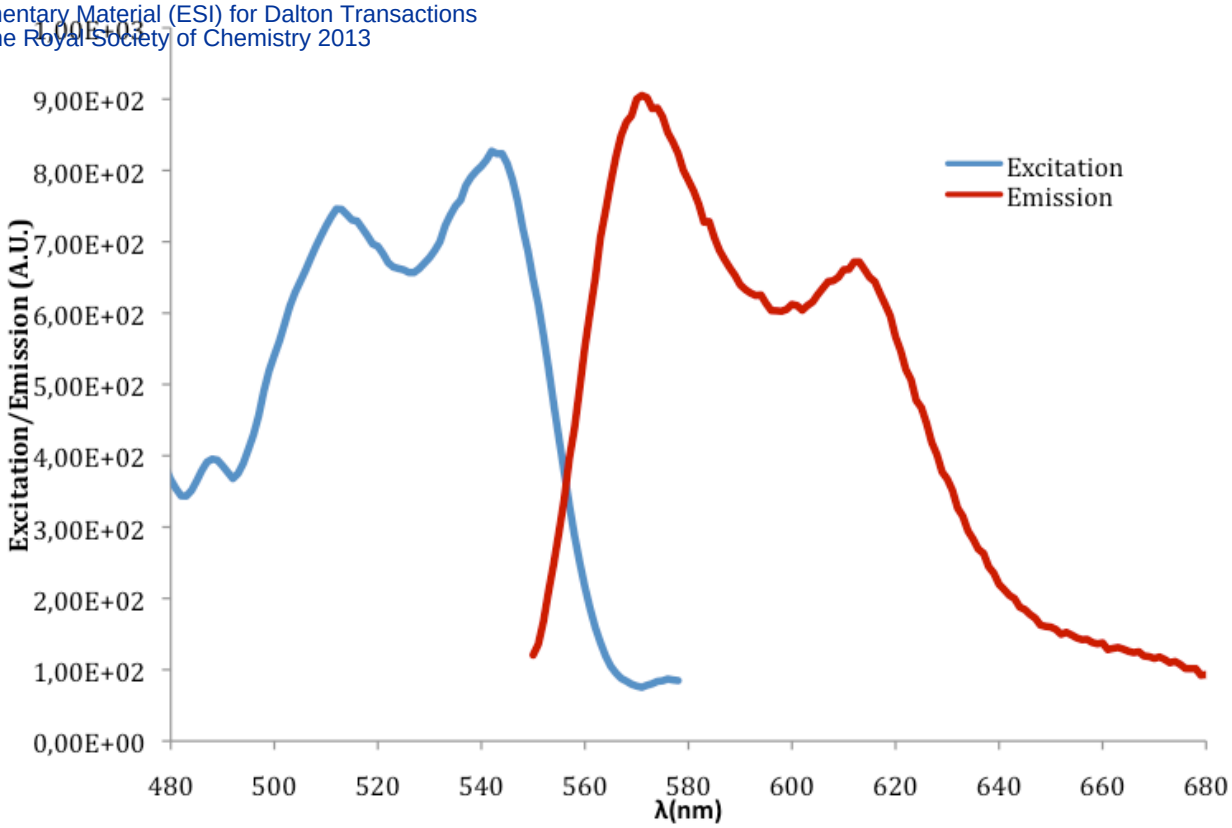
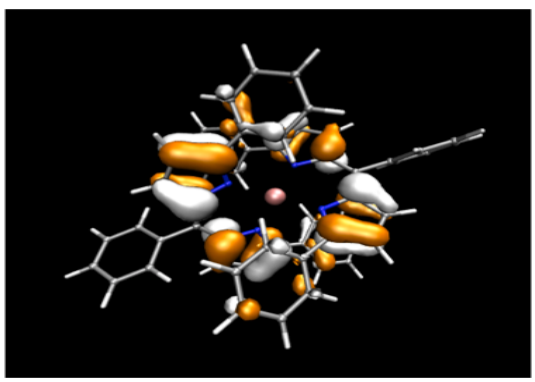
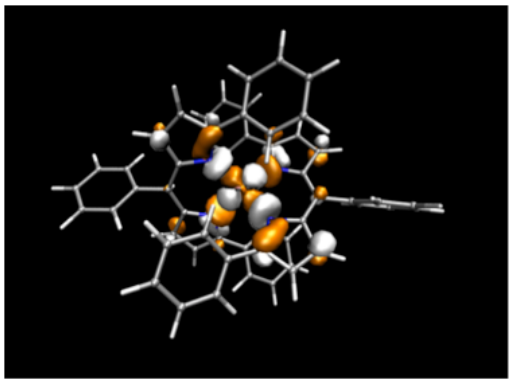


Figure S14: Excitation spectrum in blue and emission spectrum in red of $Cu(dpdipy)_2$ at 80K in EtOH/MeOH 4/1.

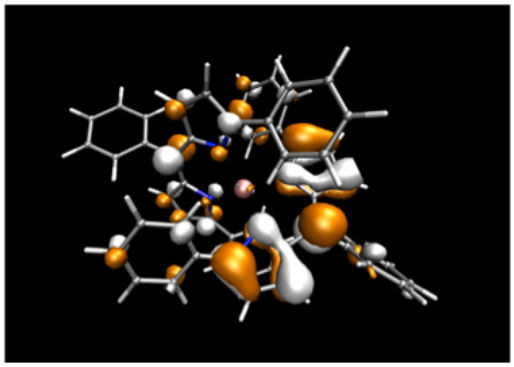
Figure S15 : The different calculated orbitals.



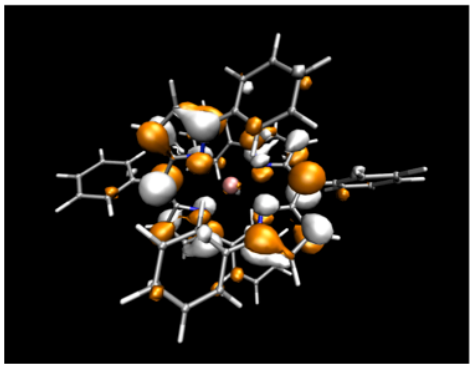
HOMO



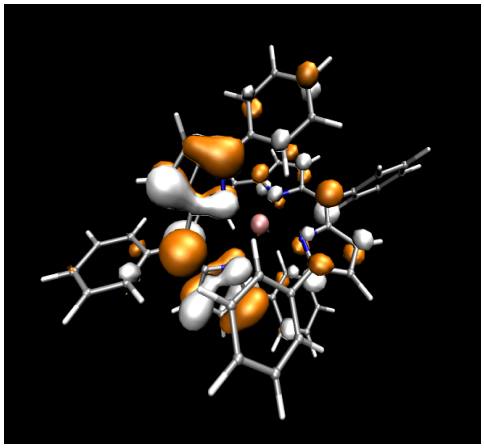
LUMO



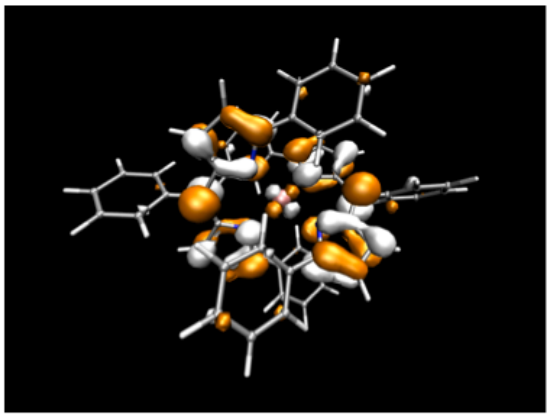
LUMO+1



LUMO+2



LUMO+3



LUMO+4

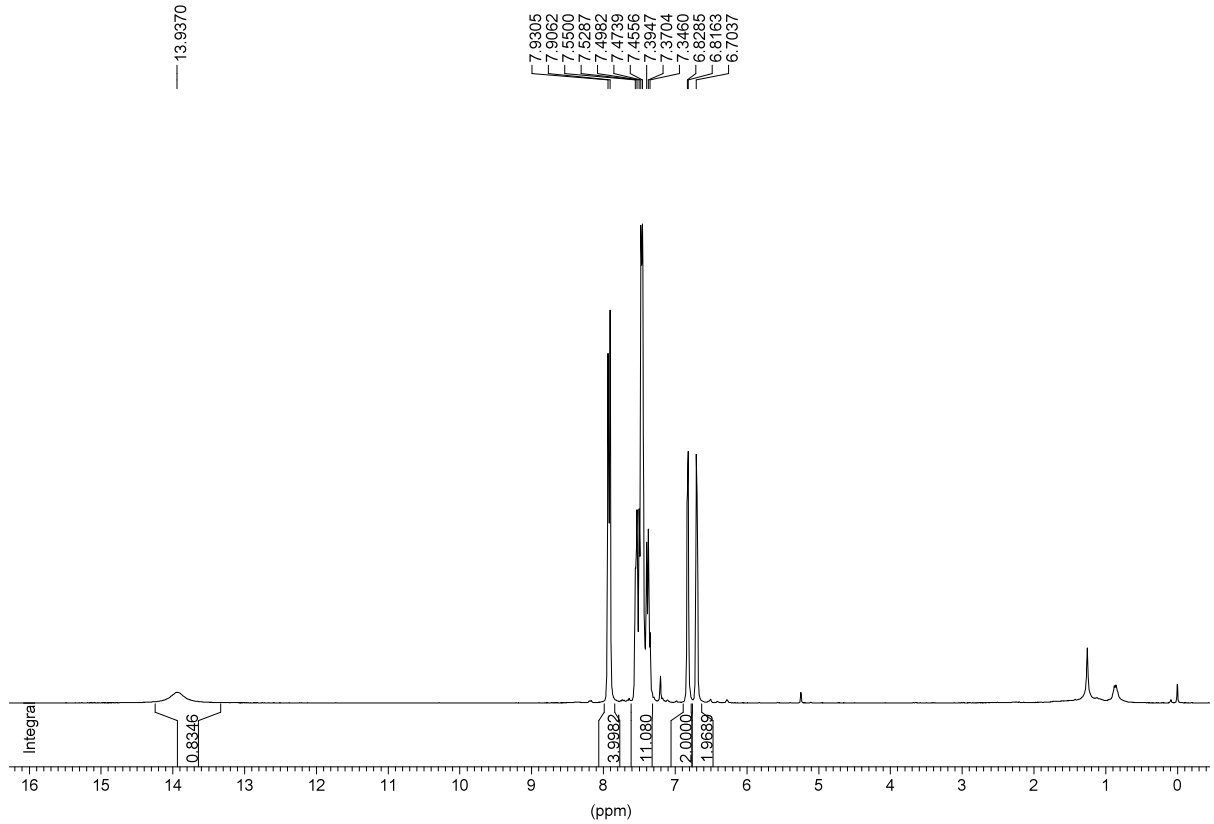


Figure S16: ^{1}H-NMR of dpdipyH ($CDCl_3$, 300 MHz, 25°C)

Supplementary Information

Tables

Table S1: XR data for the three samples

	$Cu(II)(dipy)_2$	$Cu(II)(dpdipy)_2$	$Cu(II)(dpdipy)_2$ from the synthesis of big crystals of Cu(I)
formula	$C_{30}\ H_{22}\ Cu\ N_4$	$C_{54}\ H_{38}\ Cu\ N_4$	$C_{54}\ H_{38}\ Cu\ N_4$
M ($gmol^{-1}$)	502.06	806.42	806.42
crystal dimensions (mm^3)	0.5 x 0.2 x 0.1	0.4 x0.3 x 0.2	0.4 x 0.4 x 0.3
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	17.0388(7)	13.7700(4)	18.9299(5)
b (Å)	15.6229(7)	13.5622(4)	10.5052(3)
c (Å)	19.7025(7)	21.6416(6)	21.7918(6)
α (deg)	90.00	90.00	90.00
β (deg)	115.496(2)	94.943(2)	113.925(2)
γ (deg)	90.00	90.00	90.00
V ($Å^{3)}$	4734.0(3)	4026.6(2)	3961.2(2)
Z	4	4	4
D_{calc} (gcm^3)	1.409	1.330	1.325
θ_{max} (deg)	71.30	71.48	70.93
λ (Å)	1.54178 (CuKα)	1.54178 (CuKα)	1.54178 (CuKα)
F(000)	2072	1676	1676
T (K)	100(2)	100(2)	100(2)
measured reflections	47610	39793	39036
unique reflections	9195	7712	7546

observed reflections ($I_o > 2\sigma(I_o)$)	6864	6382	6992
parameters refined	632	532	532
R_1	0.0468	0.0412	0.0335
ωR_2 [a,b,c]	0.1094 [a]	0.0988 [b]	0.0878[c]
R_1 (all data)	0.0686	0.0524	0.0361
ωR_2 (all data)	0.1229	0.1059	0.0901
GOOF	1.068	1.058	1.033
μ (mm^{-1})	1.500	1.097	1.115

[a] Weighting scheme as defined for Cu(II)(Dipy)$_2$: $\omega = 1 / [\sigma^2(F_o^2) + (0.0608\ P)^2 + 1.6118\ P]$, $P = (F_o^2 + 2F_c^2) / 3$

[b] Weighting scheme as defined for Cu(II)(dpDipy)$_2$: $\omega = 1 / [\sigma^2(F_o^2) + (0.0530\ P)^2 + 1.8201\ P]$, $P = (F_o^2 + 2F_c^2) / 3$

[c] Weighting scheme as defined for Cu(II)(dpDipy)$_2$: $\omega = 1 / [\sigma^2(F_o^2) + (0.0460\ P)^2 + 2.1928\ P]$, $P = (F_o^2 + 2F_c^2) / 3$

Table S2: Selected bond lengths [A°] and angles [°] for [Cu(II)(dipy)$_2$] and [Cu(II)(dpdipy)$_2$]

[Cu(II)(dipy)$_2$]		[Cu(II)(dpdipy)$_2$] /[Cu(II)(dpdipy)$_2$] from the synthesis of big crystals of Cu(I) complex	
Cu1 - N2	1.950(5)	Cu1 - N2	1.9582(16) / 1.9552(12)
Cu1 - N12	1.919(6)	Cu1 - N12	1.9690(16) / 1.9759(12)
Cu1 - N19	1.973(5)	Cu1 - N31	1.9524(16) / 1.9630(12)
Cu1 - N29	1.920(5)	Cu1 - N41	1.9711(16) / 1.9759(12)
N2 - Cu1 - N12	92.0(2)	N2 - Cu1 - N12	95.38(7) / 95.30(5)
N12 - Cu1 - N29	96.8(2)	N12 - Cu1 - N41	105.81(7) / 107.20(5)
N29 - Cu1 - N19	92.0(2)	N41 - Cu1 - N31	94.76(7) / 95.76(5)

N19	-	Cu1	-	N2	97.2(2)	N31	-	Cu1	-	N2	98.16(7) / 97.86(5)

Cu36	-	N37	1.964(6)
Cu36	-	N47	1.926(6)
Cu36	-	N54	1.979(5)
Cu36	-	N64	1.912(6)

N37	-	Cu36	-	N47	91.85(16)
N47	-	Cu36	-	N64	96.5(2)
N64	-	Cu36	-	N54	92.35(16)
N54	-	Cu36	-	N37	97.6(2)

Table S3: Values of different angles

Cu(II)(dipy)$_2$

Dihydral angle between N2Cu1N12 and N19Cu1N29 (complex of the bottom)	45.791°
Dihydral angle between N37Cu36N47 and N54Cu36N64 (complex of the top)	46.167°
Complex of the bottom	
angle between planes pyrrole N2 and pyrrole N12	1.096°
angle between planes pyrrole N19 and pyrrole N29	4.650°
Complex of the top	
angle between planes pyrrole N37 and pyrrole N47	1.712°
angle between planes pyrrole N54 and pyrrole N64	8.820°

Table S4: Values of different angles

$Cu(II)(dpdipy)_2$		**Big crystals from Cu(I) synthesis**
Dihydral angle between N2Cu1N12 and N31Cu1N41	63.043°	64.891°
angle between planes pyrrole N2 and pyrrole N12	18.137°	21.642°
angle between planes pyrrole N31 and pyrrole N41	14.804°	14.320°
angle between planes C13-C18 and pyrrole N2	29.513°	30.932°
angle between planes C25-C30 and pyrrole N12	27.872°	26.788°
angle between planes C42-C47 and pyrrole N31	36.058°	27.792°
angle between planes C54-C59 and pyrrole N41	34.569°	33.232°

		Butyronitrile		**Toluene**	
	$\lambda_{détection}$	τ (295 K)[a]	τ (110 K)[b]	τ (295 K)[b]	τ (185 K)[b]
$[Cu(II)(Dipy)_2]$	500 nm	≤ 1 ns	≤ 10 ns	≤ 10 ns	≤ 10 ns
$[Cu(II)(dpDipy)_2]$	595 nm	~1 ns	≤ 10 ns	≤ 10 ns	≤ 10 ns

Table S5: Luminescence lifetimes (τ) of excited $[Cu(II)(dipy)_2]$ and $[Cu(II)(dpdipy)_2]$. [a] Measurements performed by TCSPC with a pulsed diode laser as excitation source (measurable lifetimes ≥ 1ns, $\lambda_{excitation}$ = 439 nm). [b] Measurements with the Continuum pulsed laser (measurable lifetimes ≥ 10 ns, $\lambda_{excitation}$ = 480 nm).

	[Cu(II)(dpdipy)$_2$]
Cu1 – N2	2.002
Cu1 – N12	2.009
Cu1 – N31	2.005
Cu1 – N41	2.009
N2 – Cu1 – N12	94.79
N2 – Cu1 – N31	103.34
N2 – Cu1 – N41	131.91
N12 – Cu1 – N31	131.36
N12 – Cu1 – N41	106.17
N31 – Cu1 – N41	94.45

Table S6: Selected bond lengths (Å) and angles (°) of [Cu(II)(dpdipy)$_2$] optimized in gas phase at DFT/B3LYP level with the basis 6-31G* (for the atoms C, N and H) and the Stuttgart pseudopotentiel (for the Cu atom). The calculated bond length distances Cu-N and angles are consistent with the experimental values. The mean absolute errors are 0.044 Å and 1.61° for the bond length and angle respectively, while the largest discrepancy is 0.053 Å and 5.18°, respectively.

Table S7: Cartesian Coordinates (in Å) of the equilibrium geometry of [Cu(II)(dpdipy)$_2$].

Atom	X	Y	Z
C	-8.65440657	9.25350399	-16.82092470
C	-10.03811025	9.22057177	-16.48390301
C	-10.12312413	8.77919788	-15.18328648
C	-8.78895927	8.52008783	-14.73999684
C	-8.42294172	8.07940654	-13.45380732

C	-7.11849203	7.83814048	-12.98239333
C	-6.76866275	7.37423147	-11.67686292
C	-5.39791581	7.24389867	-11.64818561
C	-4.92114990	7.60201837	-12.94112861
C	-8.13890254	9.76096473	-18.10137833
C	-8.86387371	9.50598685	-19.28073157
C	-8.44831177	10.02701979	-20.50347434
C	-7.30028369	10.81923342	-20.57450170
C	-6.57428985	11.08393684	-19.41205652
C	-6.98901976	10.56441174	-18.18688110
C	-9.53798080	7.84158833	-12.48122370
C	-10.45005165	6.79459641	-12.68209715
C	-11.48138286	6.56705243	-11.77001390
C	-11.61950526	7.38628291	-10.64794916
C	-10.71968770	8.43389096	-10.44238961
C	-9.68416783	8.65926488	-11.35027667
C	-3.51654122	7.48451259	-13.36122619
C	-3.15422148	6.95957822	-14.61374142
C	-1.81296214	6.77643627	-14.94678813
C	-0.80608759	7.11139196	-14.03988960
C	-1.15251988	7.63206420	-12.79089080
C	-2.49183739	7.81188825	-12.45382874
C	-5.85525204	6.92241416	-18.10642650
C	-5.16953171	6.80184235	-19.34880578
C	-4.11687888	7.68891846	-19.31324648
C	-4.17073478	8.35399915	-18.04943789
C	-3.26822862	9.33591741	-17.59464580
C	-3.37854171	10.08927179	-16.40899228
C	-2.41064676	11.00729827	-15.89786148

C	-2.93222114	11.54217859	-14.73977036
C	-4.21402221	10.95303559	-14.55358525
C	-6.98944542	6.08033626	-17.69978009
C	-7.91645400	5.65448167	-18.66967537
C	-8.96563936	4.80314710	-18.33184219
C	-9.10918081	4.35437166	-17.01680484
C	-8.19447614	4.76530837	-16.04487707
C	-7.14412040	5.61765434	-16.38133511
C	-2.07319878	9.60848325	-18.45446048
C	-1.12935204	8.60112934	-18.71050106
C	0.18769910	10.12621695	-20.04948342
C	-0.00669001	8.85931024	-19.49685733
C	-0.74767063	11.13404701	-19.80899450
C	-1.86613950	10.87910446	-19.01512781
C	-5.15797657	11.32416712	-13.49080748
C	-6.53984791	11.41988987	-13.72804007
C	-7.40825951	11.83942786	-12.72159867
C	-6.91512458	12.17461707	-11.45871364
C	-5.54252413	12.08917872	-11.21109843
C	-4.67351327	11.67202595	-12.21624027
Cu	-5.91017549	8.67194532	-15.61060527
H	-10.84570904	9.54961823	-17.12396135
H	-11.01697916	8.66846098	-14.58673113
H	-7.46376678	7.14773938	-10.88148127
H	-4.78715795	6.87518788	-10.83463386
H	-9.74854344	8.87757804	-19.23243663
H	-5.68348576	11.70492635	-19.45583871
H	-6.42622367	10.79881606	-17.28918474
H	-10.33941055	6.15722802	-13.55474154

H	-12.17610339	5.74765891	-11.93583939
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