Supporting Information

Intramolecular Metal-Ligand Electron Transfer Triggered by Co-Ligand Substitution

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6) Visualization of the structural differences and RMSD values between the closedshell singlet state, $[Cu^{I}-1^{2+}-Cu^{I}]$, and the triplet state, $[Cu^{II}-1-Cu^{II}]$, for complexes $[1{CuCl(L)}_2]^{2+}$ (L = neutral ligand) and $[1{CuCl(X)}_2]$ (X = anionic ligand) from B3LYP/def2-SVP calculations 1) Analytical data for $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$.



Figure S1: Temperature dependent ¹H NMR spectra in CH₃CH₂CN (propionitrile) solution.



Figure S2. EPR spectra (9.63541 GHz) of $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$ at room temperature and in a frozen CH₃CN solution at 35 K: RT: $g_1 = 2.128$ and $g_2 = 2.060$, A ≈ 60 G. 35 K: $g_1 = 2.2242$ and $g_2 = 2.0613$ with A ≈ 169 G.



Figure S3. EPR spectra recorded for solid $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$ at different temperatures. At 35 K: $g_1 = 2.2322$ and $g_2 = 2.0568$ with A ≈ 158 G. 120 K: g = 2.0572. RT: $g_1 = 2.3527$ and $g_2 = 2.0539$ with A ≈ 166 G.



Figure S4. Comparison between the SQUID magnetometric curves for the chain polymer $\{[1(CuCl)_2](SbF_6)_2\}_n$ (2nPhCN) and the molecular complex $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$.

A (Bleaney-Bowers) fit was attempted, based on the spin Hamiltonian

 $H^{s} = -2J \cdot S_{Cu1} \cdot S_{Cu2}$

Due to the symmetric structure, the g values for the unpaired electrons at the two Cu^{II} atoms were assumed to be equal (g_{Cu}).

The measured $\chi_m T$ vs. T curve was then fitted with the simple equation

$$\chi_{m} \cdot T = x \cdot \left(\frac{2 \cdot N_A \cdot \mu_B^2 \cdot g_{Cu}^2 \cdot T}{k \cdot (T - \Theta_W) \left(3 + \exp\left(-\frac{J}{k \cdot T}\right)\right)} + TIP \cdot T \right)$$

(TIP = temperature-independent paramagnetism, Θ_W : Weiss temperature, J: coupling constant).

The factor x in the formula is necessary since only a fraction of the complex units $[1(CuCl)_2(CH_3CN)_2]^{2+}$ is present in the $[Cu^{II}-1-Cu^{II}]$ form, while the largest part is in the diamagnetic $[Cu^{I}-1^{2+}-Cu^{I}]$ form.

Fit for $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$:



The *J* value is in line with that estimated for other dinuclear Cu^{II} complexes with redox-active bridging guanidine ligands (see e.g. ref. 31a in the main text) On the other hand, the value for the TIP is high, indicating limits of the applied simple fit formula. We also tried a formula with an additional term that considers a small amount of "noncoupled" species (with ρ being the molar fraction of noncoupled species), but this gave no improvement concening the TIP. A possible reason for the large TIP value might be some small degree of temperature-induced valence-tautomerism in the solid state. However, the effect is small and therefore no definite conclusion on this issue is possible.



Figure S5 a) and b). Temperature-dependent UV/Vis spectra for $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$ in CH₃CN solution in different temperature ranges (a: room temperature to -40°C; b)-20°C to 70°C).



Figure S5 c) CV curve of $[1{CuCl(CH_3CN)}_2](SbF_6)_2$ measured in CH₃CN, the SCE potentials are given relative to Fc⁺/Fc, with Bu₄NPF₆ as supporting electrolyte and 100 mVs⁻¹ scan speed. CV curves recorded in a limited potential window around the redox process are drawn in red colour.



Figure S6. Temperature-dependent UV/Vis spectra for $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$ in CH_3CH_2CN (propionitrile) solution.



Figure S7. Comparison between the spectra for $[1(CuCl)_2]$ with neutral ligand unit and for $[1(CuCl)_2(CH_3CN)_2](SbF_6)_2$ at room temperature and at low temperature (-75 °C)

2) Analytical data for $[1(CuCl)_2(py)_2](SbF_6)_2$



Figure S8. UV/Vis spectrum for $[1(CuCl)_2py_2](SbF_6)_2$ in pyridine solution.



Figure S9. EPR spectra of $[1(CuCl)_2(py)_2](SbF_6)_2$ in CH₃CN solution at different temperatures. a) At room temperature only a very weak signal is detected. b) In frozen CH₃CN solution at 35 K, a strong and broad signal is observed (g_{iso} = 2.1079).



Figure S10. Temperature-dependent EPR spectra of $[1(CuCl)_2(py)_2](SbF_6)_2$ in pyridine solution at 35 K: $g_1 = 2.2586$ with A ≈ 160 G and $g_2 = 2.0849$. Further hyperfine coupling to the nitrogen nuclei (≈ 14 G) is visible. RT: $g_1 = 2.1515$ with ca. 58 G and $g_2 = 2.0871$.



Figure S11: EPR spectra of $[1(CuCl)_2(py)_2](SbF_6)_2$ in the solid state at different temperatures. 35 K: $g_1 = 2.2486$ and $g_2 = 2.0662$ with A \approx 116 G. 120 K: $g_1 = 2.2485$ and $g_2 = 2.0675$ with A \approx 114 G Room temperature: $g_1 = 2.2501$, A \approx 131 G and $g_2 = 2.0718$.



Figure S12. Comparison between the powder diffraction measurement for $[1(CuCl)_2(py)_2](SbF_6)_2$ at room temperature and the simulation of the diffractogramm from the single-crystal X-ray diffraction analysis. The comparison shows that the powder phase does not contain another microcrystalline species. Hence the second valence tautomer, that is present in the powder, is X-ray amorphous.

3) Analytical data for ${[1(CuCl)_2](SbF_6)_2}_n \cdot (2nPhCN)$.



Figure S13. Powder X-ray diffraction measurements at different temperatures.



Figure S14. Thermogravimetric curve for $\{[1(CuCl)_2](SbF_6)_2\}_n \cdot (2nPhCN)$: The first step at 150 - 182 °C (15%) is due to loss of the 2 eq. of PhCN. The compound is then stable up to 245 °C. At higher temperatures, further mass loss in two steps (10% and 35% loss) is observed until 330 °C. Temperature-dependent powder diffraction measurements for the chain polymer $\{[1(CuCl)_2](SbF_6)_2\}_n \cdot (2nPhCN)$.



Figure S15. a) Powder diffractogramm at RT. b) Powder diffractogramm at 200 °C.



Figure S16. Temperature dependent EPR spectra of the polymer in the solid state. 35 K: $g_1 = 2.2296$ with A \approx 143 G and $g_2 = 2.0569$. RT: $g_1 = 2.2441$ with A \approx 124 G and $g_2 = 2.0589$.

Conductivity measurements

Table S1. R values obtained as slopes from linear fits of the V/I curves) for severaltemperatures.

1/T	R (ΔU/ΔΙ) [Ω]	-ln(1/R)
0.00207125	5.54·10 ⁷	17.8302872
0.00207254	6.09 [.] 10 ⁷	17.9249248
0.0020734	6.42 [.] 10 ⁷	17.9776969
0.00208899	8.81·10 ⁷	18.2944616
0.00211416	14.0·10 ⁷	18.7582413
0.00216169	32.5·10 ⁷	19.5993677
0.00221092	73.6·10 ⁷	20.4161693
0.00225632	418.91·10 ⁷	22.1557487
0.00225887	444.97·10 ⁷	22.2161017
0.00231107	770.42·10 ⁷	22.7650371
0.00231911	804.28·10 ⁷	22.808049
0.00236072	1615.22·10 ⁷	23.5053209
0.00241955	3121.76·10 ⁷	24.1642492
0.00242189	3051.33·10 ⁷	24.1414286
	1/T 0.00207125 0.00207254 0.0020734 0.00208899 0.00211416 0.00216169 0.00221092 0.00225632 0.00225887 0.00231107 0.00231911 0.00236072 0.00241955 0.00242189	1/TR (ΔU/ΔI) [Ω]0.002071255.54·1070.002072546.09·1070.00207346.42·1070.002088998.81·1070.0021141614.0·1070.0021616932.5·1070.0022109273.6·1070.00225632418.91·1070.00231107770.42·1070.00231911804.28·1070.002360721615.22·1070.002419553121.76·1070.002421893051.33·107

4) Details of the crystal structure determinations of $[1{CuCl(CH_3CN)}_2](SbF_6)_2$, $[1{CuCl(py)}_2](SbF_6)_2$, $\{[1(CuCl)_2](SbF_6)_2\}_n \cdot (2nPhCN)$ and $[Cu(map)_3]Cl_2$.

Table S2. Details of the crystal structure determinations of $[1{CuCl(CH_3CN)}_2](SbF_6)_2$, $[1{CuCl(py)}_2](SbF_6)_2$, ${[1(CuCl)_2](SbF_6)_2}_n \cdot (2nPhCN)$ and $[Cu(map)_3]Cl_2$.

	$[1{CuCl(CH_3CN)}_2]$ $(SbF_6)_2$	[1 {CuCl(py)} ₂] (SbF ₆) ₂	{[1 (CuCl) ₂](SbF ₆) ₂ } _n · (2nPhCN)	[Cu(map) ₃]Cl ₂
formula	$\begin{array}{c} C_{30}H_{56}CI_{2}Cu_{2}F_{12}N_{14}\\ Sb_{2} \end{array}$	$\begin{array}{c} C_{36}H_{60}CI_{2}Cu_{2}F_{12}N_{14}\\ Sb_{2} \end{array}$	$\begin{array}{c} C_{40}H_{60}CI_{2}Cu_{2}F_{12}N_{14}S\\ b_{2} \end{array}$	$C_{24}H_{34}CI_2CuN_8O$
crystal system	orthorhombic	monoclinic	orthorhombic	triclinic
space group	P bcn	<i>P</i> 2(1)/n	P ccn	<i>P</i> -1
a /Å	16.08984(16)	12.210(2)	11.12549(13)	10.6115(4)
b/Å	18.88601(13)	17.004(3)	22.2307(3)	11.2052(4)
c /Å	15.90472(14)	12.728(3)	21.9849(3)	12.3212(6)
α /°				69.734(4)
βl°		93.36(3)		89.956(3)
γ l°				82.315(3)
V /Å ³	4833.01(7)	2638.0(9)	5437.48(11)	1360.36(10)
Ζ	4	2	4	2
<i>M</i> _r	1282.36	1358.46	1406.50	585.03
F ₀₀₀	2544	1352	2800	610
d _c /Mg⋅m ⁻³	1.762	1.710	1.718	1.428
μ /mm ⁻¹	2.171	1.994	1.938	3.208
max., min. transmission factors	0.872, 0.760 ª	0.6355, 0.5421	0.927, 0.787 ª	0.7930, 0.7836 ^b
X-radiation, λ /Å	Μο- <i>Κ</i> α, 0.71073	Mo- <i>K</i> α, 0.71073	Mo- <i>K</i> α, 0.71073	Cu- <i>K</i> α, 1.54184
data collect. temperat. /K	120(1)	120(1)	120(1)	120(1)
heta range /°	3.0 to 32.4	2.00 to 30.06	2.6 to 32.4	3.8 to 71.6
index ranges h,k,l	-23 23, -28 28, -23 23	-17 17, -23 23, -17 17	-16 16, -33 33, -33 33	-12 12, -13 13, -14 15
reflections measured	174732	44138	176887	42653
unique [R _{int}]	8562 [0.0497]	7716 [0.0637]	9622 [0.0706]	5175 [0.0502]
data / restraints /parameters	8562 / 154 / 292	7716 / 0 / 315	9622 / 144 / 334	5175 / 51 / 325
GooF on F ²	1.041	1.014	1.044	1.070
R indices [F>4□(F)] R(F), wR(F²)	0.0454, 0.1026	0.0396, 0.0861	0.0371, 0.0798	0.0515, 0.1353

	[1{CuCl(CH ₃ CN)} ₂] (SbF ₆) ₂	[1 {CuCl(py)} ₂] (SbF ₆) ₂	{[1 (CuCl) ₂](SbF ₆) ₂ } _n · (2nPhCN)	[Cu(map)₃]Cl ₂
R indices (all data) R(F), wR(F²)	0.0562, 0.1077	0.0759, 0.1003	0.0558, 0.0864	0.0644, 0.1438
largest residual peaks /e·Å ⁻³	3.079, -2.506	1.017, -0.720	1.009, -0.696	1.130, -0.829

^a Numerical absorption correction. ^b Empirical absorption correction.

5) Descriptions of further ligand substitution experiments



Results of Evans NMR studies for the reaction of [1{CuCl(CH₃CN)}₂](SbF₆)₂ with Et₄NCl

Figure S17: Results of the Evans-NMR studies for the reaction of $[1{CuCl(CH_3CN)}_2](SbF_6)_2$ with Et₄NCI. The measurements were carried out in a CH₂Cl₂ solution at 30 °C.

Table S3: Results of the Evans-NMR studies for the reaction of $[1{CuCl(CH_3CN)}_2](SbF_6)_2$ with Et₄NCl.

equivalents	c([1(CuCl ₂) ₂]	δν [Hz]	μ _{eff} [μ _B]	χмΤ
Et₄NCI	[g/cm ³]			[cm ³ K mol ⁻¹]
0.0	0	0	0.00	0.00
0.4	0.0021	1	1.05	0.21
0.8	0.0041	2	1.07	0.23
1.2	0.0060	3	1.08	0.23
1.6	0.0076	4	1.10	0.24
2.0	0.0095	5	1.11	0.25

The relatively low μ_{eff} value after addition of two equivalents of Et₄NCI presumably results from valence-tautomeric equilibria in solution. The addition of the salt

increases the ionic strength of the solution and thereby shifts the equilibrium towards the diamagnetic $[Cu^{I}-1^{2+}-Cu^{I}]$ form (see ref. 31a in the main text for a discussion of this issue). This effect is not visible in the UV/Vis experiments due to the much lower concentrations.

<u>Reaction between [1(CuCl)₂] and 2-(methylamino)pyridine (map, compound **G** in <u>Scheme 6):</u></u>



Figure S18. Illustration of the structure of the dicationic complex $[Cu(map)_3]^{2+}$ (map = 2-(methylamino)pyridine) with two chloride anions, obtained from oxidation of $[1(CuCl)_2]$ with NO(SbF₆) in map. Anisotropic displacement ellipsoids drawn at the 50% probability level.

Substitution test with NaOMe

Compound **1** (55 mg, 0.104 mmol) and CuCl (20 mg, 0.202 mmol) are dissolved in 5 ml CH₃CN. The yellow-coloured reaction mixture is stirred at room temperature for 1 h. Then a solution of $NOSbF_6$ (54 mg, 0.202 mmol) in 4 ml CH₃CN is added and the reaction mixture is stirred for additional 30 min. After addition of sodium methoxide (0.06 ml, 5.4 molar in methanol) the formation of a brown precipitate is

observed. It is filtered, washed twice with 1 ml portions of diethylether and dried under vacuum. The conversion was followed by UV/Vis-experiments.



Scheme S1. Ligand substitution induced intramolecular metal-ligand electron transfer.



Figure S19. UV/Vis-spectra of the substitution experiment with sodium methanolate in acetonitrile.

Substitution experiments with other neutral ligands L.

In further substitution experiments it is attempted to substitute the weakly bound CH₃CN ligands in [1{CuCl(CH₃CN)}₂]²⁺ by 2-(methylamino)pyridine (map), to stabilize the (Cu^{II}-1-Cu^{II}] form by a higher coordination number. However, the salt [Cu^{ll}(map)₃]²⁺(Cl⁻)₂ with octahedrally coordinated copper crystallizes from the reaction mixture, showing that oxidation to Cu^{II} in this case is accompanied by cleavage of the guanidine-copper bond. Hence, the ligand substitution indeed stimulates an electron transfer reaction in which copper is oxidized (Cu^I \rightarrow Cu^{II}) and obviously the guanidine ligand reduced $(1^{2+} \rightarrow 1)$, as sketched in Scheme 4, but nevertheless the expected product $[1{CuCl(map)}_2]^{2+}$ is not obtained. In another sodium methanolate is added stepwise experiment, to a solution of $[1{CuCl(CH_3CN)}_2](SbF_6)_2$ in CH₃CN to obtain the neutral complex $[1{CuCl(OMe)}_2]$. The methanolate ligands should favor Cu^{II}. In the UV/Vis spectra, the intense absorption band at 427 nm due to 1^{2+} disappears during addition of methanolate. Simultaneously, a new intense absorption grows in at 306 nm, indicating conversion of a [Cu^I-1²⁺-Cu^I] type complex into its [Cu^{II}-1-Cu^{II}] form. Unfortunately, the isolation of a clean product is not achieved, but the analytical data point to a metal-ligand electron transfer initiated by substitution.

6) Results of the quantum chemical calculations on the complexes $[1{CuCl(L)}_2]^{2+}$ (L = neutral ligand) and $[1{CuCl(X)}_2]$ (X = anionic ligand)

The following pictures (made with the *aRMSD* program) illustrate the structural differences of the closed-shell singlet form $[Cu^{I}-1^{2+}-Cu^{I}]$ and the triplet state of the $[Cu^{II}-1-Cu^{II}]$ form. The sizes of the sphere radii at the nuclear coordinates are proportional to the relative contribution of the respective atom pair to the total RMSD. The absolute RMSD value for each pair is given by the sphere color on a red-yellow-green (RYG) scale with a default range from ≥ 0.7 Å to 0.0 Å. For further information on the *aRMSD* program (freeware), see: A. Wagner, H.-J. Himmel, *J. Chem. Inf. Model.* **2017**, 57, 428–438



Figure S20. a) Superpositions of the closed-shell singlet and triplet structures of L= PCy_3 (Ligand A) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. b) Superpositions of the closed-shell singlet and triplet structures of L= MeCN (Ligand B) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. c) Superpositions of the closed-shell singlet and triplet structures of L= 2-DMAP (Ligand C) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. d) Superpositions of the closed-shell singlet and triplet structures of L= DABCO (Ligand D) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. e) Superpositions of the closed-shell singlet and triplet structures of L= Pyridine (Ligand E) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. f) Superpositions of the closed-shell singlet and triplet structures of L= Carbene (Ligand F) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. g) Superpositions of the closed-shell singlet and triplet structures of L= Pycolylamin (Ligand G) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).

g)



Figure S20. h) Superpositions of the closed-shell singlet and triplet structures of L= 4-DMAP (Ligand H) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).

i) SCN (ligand I, Scheme 5)

B3LYP

RMSD: Å



Figure S20. i) Superpositions of the closed-shell singlet and triplet structures of X= SCN⁻ (Ligand I) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color). The RMSD-Value is 0.548770 Å.



Figure S20. j) Superpositions of the closed-shell singlet and triplet structures of X= OMe⁻ (Ligand J) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).



Figure S20. k) Superpositions of the closed-shell singlet and triplet structures of X= CI⁻ (Ligand K) from B3LYP/def2-SVP calculations arranged according to increasing Root-Mean-Square-Deviation (RMSD) values (given below in Table S2.). The sphere dimensions reflect the relative RMSD distribution and the color code the absolute deviation (small for green color and large for red color).

k)

Barrier for valence tautomerization:

Obviously, it is much more difficult to estimate trends in the barriers for valence tautomerism. The distortion of the coordination mode from square planar (Cu^{II}) respectively tetrahedral (Cu^I) at the Cu atom leading to a structural harmonization of the two valence tautomers might be a suitable indicator for trends concerning the intrinsic barrier. In the following discussion, the dihedral angle κ between the N-Cu-N plane involving the guanidine N atoms and the L/X-Cu-Cl plane involving the first atom of the L respectively X ligand, is considered as parameter (see Table S3). Furthermore, the τ_4 value ($\tau_4 = (360 - \alpha - \beta)/141$, where α and β denote the two largest angles at the copper atom and 141 is a scaling factor that provides $\tau_4 = 1$ for tetrahedral and 0 for square-planar coordination)^[1] is included in Table S2. As expected, the dihedral angles are larger for the closed-shell singlet than for the triplet states. However, the differences are small, ranging from 7.84° for X = OMe (J) to 22.44° for L = carbene (F). These small differences are to the most part due to the large dihedral angles in the triplet states (56.46° - 67.65°), in line with previously experimentally determined dihedral angles in related complexes and other Cuguanidine complexes ^[2] Consequently, τ_4 values higher than 0.5 are found for all complexes. Obviously, these parameters only consider the structure at the copper atom. Therefore the root-mean-square deviation (RMSD) between the structures of the closed-shell singlet and triplet states are calculated using the aRMSD program.^[3] The complexes with pyridine (ligand E) and acetonitrile (ligand B) ligands exhibit quite low RMSD values. Higher RMSD values are found for the neutral related ligands C, H, and the anionic ligand J, but still the values indicate in all cases relatively small structural differences between the two valence tautomers.

Hence the calculations indicate a low intrinsic barrier for electron transfer between ligand and metal. However, it should be emphasized that the extrinsic barrier (caused by solvent reorganization) are not included in these calculations.

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Table S3. Comparison between the structures of the closed-shell singlet and the open shell triplet states of $[1{CuCl(L)}_2]^{2+}$ respectively $[1{CuCl(X)}_2]$ (see Scheme 5 for the L/X abbreviations), the dihedral angle κ , the τ_4 value and the root-mean square deviation (RMSD).

L/X	к	τ ₄	RMSD /	
			Å	
B (singlet)	76.52	0.7881	0.4505	
B (singlet)	56.46	0.5529	0.4585	
C (singlet)	76.73	0.8225	0 700 4	
C (triplet)	65.54	0.6594	0.7324	
D (singlet)	76.51	0.7514	0 4071	
D (triplet)	67.65	0.6572	0.4971	
E (singlet)	77.5	0.7465	0 5109	
E (triplet)	61.45	0.6096	0.5108	
F (singlet)	82.58	0.8292	0 4683	
F (triplet)	60.14	0.6094	0.4003	
G (singlet)	71.70	0.7920	0 4549	
G (triplet)	58.69	0.5484	0.4349	
H (singlet)	77.50	0.7516	1 0506	
H (triplet)	61.38	0.6080	1.0000	
I (singlet)	73.93	0.8240	0 5488	
I (singlet)	61.18	0.6130	0.0400	
J (singlet)	70.33	0.7337	0 7032	
J (triplet)	62.49	0.6182	0.7352	

Reaction with 2-(Methylamino)pyridine (map).

Compound $[1{CuCl(CH_3CN)}_2](SbF_6)_2$ (13 mg, 0.01 mmol) is dissolved in map (0.5 ml) and stirred at room temperature overnight. Meanwhile a color change from green to yellow can be observed. The yellow colored reaction mixture is filtered of and the filtrate is layered with diethylether (1 ml). After one week the formation of small blue needle shaped crystals of $[Cu(map)_3](SbF_6)_2$ can be obtained.

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