Supplementary Material (ESI) for PCCP
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Electronic Supplementary Information

for:

An integrated experimental and theoretical investigation on $Cu(hfa)_2$•TMEDA: structure, bonding and reactivity

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Table S1. Relevant bond distances *d,* NBO charges *q*, (with corresponding Mulliken charges in parenthesis) and Mulliken spin densities *S* of $[Cu(H_2O)_n(NH_3)_n]^{2+}$ (n=1, 2) optimized at different levels of theory adopting the ECP10-MDF-aug-cc-pVDZ-PP combination of pseudopotential and basis set for Cu and a D95+* for ligand atoms. For the smaller system (n=1) the Møller-Plesset MP2,[1] the coupled cluster with double substitutions (CCD)[2] and the coupled cluster with single and double substitutions (CCSD)[3] levels of theory have been compared with B3LYP; for the n=2 system only the MP2 and B3LYP levels of theory have been considered.

n=1 (C_s symmetry)	MP2	CCD	CCSD	B3LYP
d(Cu-O) (nm)	0.1830	0.1847	0.1847	0.1865
d(Cu-N) (nm)	0.1876	0.1904	0.1895	0.1908
q_{Cu}	1.765 (1.279)	1.769 (1.314)	1.767 (1.304)	1.577 (1.032)
q_O	-1.144 (-0.904)	-1.141 (-0.910)	-1.142 (-0.910)	-1.074 (-0.711)
q_N	-1.314 (-1.214)	-1.314 (-1.241)	-1.315 (-1.227)	-1.190 (-1.024)
S_{Cu}	1.027	1.024	1.025	0.981
n=2 (C_2 symmetry)	MP2	-	-	B3LYP
d(Cu-O) (nm)	0.1997	-	-	0.2027
d(Cu-N) (nm)	0.1976	-	-	0.2008
q_{Cu}	1.680 (1.554)	-	-	1.399 (1.279)
q_O	-1.098 (-0.985)	-	-	-1.049 (-0.864)
q_N	-1.252 (-1.483)	-	-	-1.163 (-1.318)
S_{Cu}	0.897	-	-	0.702

1 C. Møller and M.S. Plesset*, Phys. Rev*., 1934, **46**, 618.

2 R. J. Bartlett and G. D: Purviss, *Int. J. Quant. Chem.*, 1978, **14**, 516

3 J. C. Zek, *Adv. Chem. Phys*., 1969, **14**, 35.

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Table S2. Relevant geometrical parameters of $Cu(hfa)_2$•TMEDA optimized with the C_2 symmetry at different levels of theory.[a]

Bond lengths (nm)	*Exp*	*U-B3LYP SDD D95*	*U-B3LYP SDD* D95**	*U-B3LYP TZVP D95**	*U-B3LYP AVDZ D95+*[b]*	*U-PBE AVDZ D95+**	*U-PBE PW PW*
Cu-O(1)	0.2337(2)	0.2316	0.2313	0.2324	0.2358	0.2347	0.2328
Cu-O(2)	0.1977(3)	0.2013	0.2006	0.2008	0.2007	0.1995	0.2005
Cu-N(1)	0.2021(5)	0.2080	0.2108	0.2119	0.2083	0.2098	0.2113
N(1)-C(1)	0.1435(7)	0.1505	0.1487	0.1487	0.1492	0.1490	0.1489
O(1)-C(7)	0.1236(5)	0.1275	0.1250	0.1250	0.1246	0.1259	0.1255
O(2)-C(9)	0.1244(5)	0.1293	0.1268	0.1269	0.1267	0.1280	0.1276
C(7)-C(8)	0.1425(6)	0.1418	0.1418	0.1418	0.1420	0.1423	0.1415
C(8)-C(9)	0.1377(5)	0.1400	0.1399	0.1399	0.1398	0.1404	0.1396
Bond angles							
O(1)-Cu-	84.67(10)	86.9	84.7	84.7	83.4	85.6	85.4
O(1)-Cu-	94.90(14)	97.4	96.0	96.0	94.1	91.6	95.6
O(2)-Cu-	90.72(12)	91.7	91.4	91.4	91.6	91.2	91.2
O(1)-Cu-	159.66(12)	165.6	168.4	168.4	163.6	168.9	169.5
O(2)-Cu-	174.76(16)	179.2	177.5	177.1	178.0	177.1	177.4
Cu-O(1)-	118.7(2)	122.0	120.7	120.6	120.5	118.6	119.4
Cu-O(2)-	128.5(3)	129.4	127.9	128.0	129.2	126.6	126.8
Cu-N(1)-	107.9(3)	108.6	104.9	105.0	105.2	104.6	104.4

[a]The level of calculation is specified on top of the table, *i.e.*: line 1: DFT functional; line 2: Cu pseudopotential and basis set; line 3: ligands basis set. For Cu, the notation AVDZ refers to ECP10-MDF-aug-cc-pVDZ-PP. All structures are optimized in the gas phase except from [b].

[b] Optimization performed adopting the PCM solvent model (ethanol).

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For comparison, the corresponding experimental values are reported in the second column.

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Table S3. FT-IR bands assignment. Legends: ν = stretching, β = in plane bending, γ = out of plane bending, δ_{as} = asymmetric deformation, δ_s = symmetric deformation, rock = rocking mode, wag = wagging mode, twist = twisting mode. Bold characters indicate the normal mode dominant component. For atom labels, see Figure S1.

Exp (cm^{-1})		*assignment*
3135	→	ν(CH) hfa
3027	→	ν(CH_b) TMEDA
3000 - 2900	→	ν(CH_b) + ν($CH_{b'}$) TMEDA
2880 - 2810	→	ν($CH_{a'}$) + ν(CH_a) TMEDA
1674	→	**ν(C=O)** + ν(C=C) hfa
1549	→	**ν(C=C)** + β(C-H) hfa
1527	→	**β(C-H)** + ν(C=C) + ν(C=O) hfa + δ(CH_2) (scissor) + δ_{as}(CH_3) TMEDA
1505	→	**β(C-H)** + ν(C=C) + ν(C=O) hfa + δ(CH_2) (scissor) + δ_{as}(CH_3) TMEDA
1480, 1468	→	δ_{as}(CH_3) TMEDA
1441	→	δ_{as}(CH_3) + δ_s(CH_3) TMEDA
1412	→	δ_s(CH_2) (wag) TMEDA
1384	→	δ_{as}(CH_2) (wag) TMEDA
1338	→	ν_s(C-CF_3) hfa
1313, 1287	→	δ_{as}(CH_3) + δ_{as}(CH_2) (twist) TMEDA
1257	→	β(C-H) + ν_s(C-CF_3) hfa
1210, 1186	→	ν_s(C-F) (mainly C-F_c bonds) hfa
1140	→	β(C-H) + ν_s(C-CF_3) + $\nu_{s,as}$(C-F) (all bonds) hfa
1106	→	δ_s(CH_3) + δ_s(CH_2) (twist) TMEDA
1086	→	ν_s(C-C) + $\nu_{s,as}$(C-F) (not involving C-F_c bonds) hfa
1059	→	ν(C-C) + δ(CH_2) (wag) TMEDA
1047	→	ν(C-C) + δ_{as}(CH_3) + δ(CH_2) (rock/twist) TMEDA
1020	→	**ν(C-N)** + ν(C-C) +δ_{as}(CH_3) + δ(CH_2) (rock/twist) TMEDA
1003	→	**δ(CH_2)** (rock) + δ_{as}(CH_3) + ν(C-N) TMEDA
952	→	ν(C-N) + δ_{as}(CH_3) + δ(CH_2) (rock) TMEDA
939	→	**ν_s(C-C)** + ν(C-CF_3) + ν(C-F) hfa
922	→	TMEDA symmetric breathing + δ(CH_2) (rock) + δ(CH_3)
790, 810	→	**γ(C-H)** hfa + TMEDA symmetric breathing + δ(CH_2) (wag) + ν(C-F), ν(C-C) hfa
760, 766	→	γ(C-H) hfa; ν(C-N) + ν(C-C) + δ(CH_2) (rock) TMEDA
738, 699	→	δ(CF_3) (scissor) + ν_s(C-F) + ν(C-C) hfa
666	→	collective in plane bending hfa [ν(C-C) + δ(CF_3) (scissor)]
635	→	TMEDA asymmetric breathing/δ(CH_2) (rock)
585	→	collective in plane bending hfa [ν(C-C) + **δ(CF_3)** (scissor) + ν(Cu-O)]
576	→	collective in plane bending hfa [ν(C-C) + δ(CF_3) (scissor) + **ν(Cu-O)**]
525	→	symmetric out of plane bending hfa + δ(CF_3) (scissor)
440 - 510	→ ν(Cu-N(1)) + ligands multiband deformation modes (wag, rock, twist, scissor, breathing)]	breathing modes of N(1) N(1)* O(2) O(2)* plane [mainly ν(Cu-O(2)),

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Calculated wavenumbers: 461 cm^{-1}: ν(Cu-N) dominant, 483 cm^{-1}: equal contribution of ν(Cu-O(2)) and ν(Cu-N) modes; 491 cm^{-1}: ν(Cu-O(2)) dominant; 502 cm^{-1}: ν(Cu-N) dominant.

Table S4. UV-Vis spectral data, TD-DFT calculated excitations and approximate assignments. A graphical representation of the corresponding MOs is reported in Figures **S3-S5**.[a]

E (eV) (*exp*)	*E(eV) (calc)*	*f*	*Composition %*		*Nature of the transition and approximate assignment*
1.6-2.0 (w)	1.91	0.0003	β HOMO-6 → β LUMO	26%	$\mathbf{M}(d_z^2) \rightarrow \mathbf{M}(d_{xy}) + L_{(TMEDA\ homo,\ hfa\ lumo)}$
	2.03	0.0002	β HOMO-9 → β LUMO	49%	$\mathbf{M}(d_{xz}) \rightarrow \mathbf{M}(d_{xy}) + L$
			β HOMO-7 → β LUMO	26%	$\mathbf{M}(d_{xy}) + \mathbf{L}_{(TMEDA\ homo,\ hfa\ homo-2)} \rightarrow \mathbf{M}(d_{xy}) + L$
2.8-3.1 (w)	3.16	0.0036	β HOMO-1 → β LUMO	85%	$\mathbf{L}_{(hfa\ homo)} \rightarrow \mathbf{M}(d_{xy})$
3.5 (m)	3.44	0.0019	β HOMO → β LUMO	53%	$\mathbf{L}_{(hfa\ homo)} + M(d_{yz}) \rightarrow \mathbf{M}(d_{xy}) + L$
	3.51	0.0020	α HOMO-3 → α LUMO	28%	$\mathbf{M}(d_z^2) + \mathbf{L}_{(hfa\ homo-1)} \rightarrow \mathbf{L}_{(hfa\ lumo)}$
			β HOMO-2 → β LUMO+1	25%	$\mathbf{M}(d_z^2) + \mathbf{L}_{(hfa\ homo-1)} \rightarrow \mathbf{L}_{(hfa\ lumo)}$
4.1 (vs)	3.91	0.0275	β HOMO-3 → β LUMO	81%	$\mathbf{L}_{(hfa\ homo-1)} \rightarrow \mathbf{M}(d_{xy}) + L$
	4.07	0.0819	β HOMO-4 → β LUMO	68%	$\mathbf{L}_{(hfa\ homo-2,TMEDA\ homo-1)} + M(d_z^2) \rightarrow \mathbf{M}(d_{xy}) + L$
4.4-4.6 (vs)	4.43	0.1190	β HOMO-8 → β LUMO	28%	$\mathbf{M}(d_z^2) \rightarrow \mathbf{M}(d_{xy}) + L$
	4.51	0.1756	β HOMO-4 → β LUMO	26%	$\mathbf{L}_{(hfa\ homo-2,TMEDA\ homo-1)} + M(d_z^2) \rightarrow \mathbf{M}(d_{xy}) + L$
			β HOMO-8 → β LUMO	23%	$\mathbf{M}(d_z^2) \rightarrow \mathbf{M}(d_{xy}) + L$
	4.54	0.0448	β HOMO-5 → β LUMO	23%	$\mathbf{L}_{(hfa\ homo-2,TMEDA\ homo)} + M(d_{xz}) \rightarrow \mathbf{M}(d_{xy}) + L$
	4.55	0.0101	α HOMO-4 → α LUMO	45%	$\mathbf{L}_{(hfa\ homo-1)} \rightarrow \mathbf{L}_{(hfa\ lumo)}$
	4.60	0.0721	α HOMO-4 → α LUMO+1	50%	$\mathbf{L}_{(hfa\ homo-1)} \rightarrow \mathbf{L}_{(hfa\ lumo)}$
	4.64	0.0806	α HOMO-4 → α LUMO	45%	$\mathbf{L}_{(hfa\ homo-1)} \rightarrow \mathbf{L}_{(hfa\ lumo)}$
4.9-5.3 (t)	4.92	0.0204	α HOMO-6 → α LUMO	35%	$\mathbf{L}_{(hfa\ homo-2,\ TMEDA\ homo)} + M(d_{xz}) \rightarrow \mathbf{L}_{(hfa\ lumo)}$
			α HOMO-5 → α LUMO+1	29%	$\mathbf{L}_{(hfa\ homo-2,TMEDA\ homo-1)} + M(d_z^2) \rightarrow \mathbf{L}_{(hfa\ lumo)}$
	5.03	0.0196	β HOMO-4 → β LUMO+2	56%	$\mathbf{L}_{(hfa\ homo-2,TMEDA\ homo-1)} + M(d_z^2) \rightarrow \mathbf{L}_{(hfa\ lumo)}$
			β HOMO-5 → β LUMO+1	33%	$\mathbf{L}_{(hfa\ homo-2,TMEDA\ homo)} + M(d_{xz}) \rightarrow \mathbf{L}_{(hfa\ lumo)}$

[a] Only transitions with predicted oscillator strengths $f > 0.01$ are cited unless a weaker transition relates to an observed feature. The reported assignments are approximate, and the dominant character of each excitation is evidenced in bold. The (L + M) notation indicates that the initial or final state of the transition is localized on both metal and ligands. Capital and lower case characters refer to $Cu(hfa)_2$•TMEDA MOs and ligands MOs, respectively. Contributions to the transitions with weights < 20% are not listed. Legends: L = ligands; *f* = calculated oscillator strength; M = Metal; w = weak intensity; m = medium intensity; vs = very strong intensity; t = tail.

Table S5[a]. Donor/acceptor perturbation energies E(2) for $Cu(hfa)_2$•TMEDA.

α spin			*β spin*		
Donor	*Acceptor*	*E(2) (kJ/mol)*	*Donor*	*acceptor*	*E(2) (kJ/mol)*
Cu	TMEDA		Cu	TMEDA	
Lp*[0.129]	Ry*(N(1))	32.6	Lp*[0.133]	Ry*(N(1))	19.7
Lp*[0.129]	Ry*(N(1))*	32.6	Lp*[0.133]	Ry*(N(1))*	19.7
Cu	hfa		Cu	hfa	
Lp*[0.129]	Ry*(O(1))	-	Lp*[0.133]	Ry*(O(1))	-
Lp*[0.129]	Ry*(O(2))	22.6	Lp*[0.133]	Ry*(O(2))	22.6
TMEDA	Cu		TMEDA	Cu	
Lp(N(1))	Lp*	43.9	Lp(N(1))	Lp*	105.4
Lp(N(1))*	Lp*	43.9	Lp(N(1))*	Lp*	105.4
hfa	Cu		hfa	Cu	
Lp(O(1))	Lp*	31.0	Lp(O(1))	Lp*	30.1
Lp(O(2))	Lp*	70.7	Lp(O(2))	Lp*	158.6

[a]Only contributions with E(2) > 4.2 kJ/mol and energy difference between the donor and acceptor NBO orbitals $\Delta\varepsilon_{ij} < 0.1$ a.u. are reported. Lp = lone pair; Ry = Rydberg orbital. The * symbol refers to antibonding NBO orbitals. For the Cu-backdonation interactions, the NBO orbital populations calculated for Cu are reported in brackets.

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Figure S1. Representation of the C_2 gas phase optimized structure of $Cu(hfa)_2$•TMEDA.

Atom color codes: Cu: yellow, F: green, O: red, N: blue, C: grey, H: white.

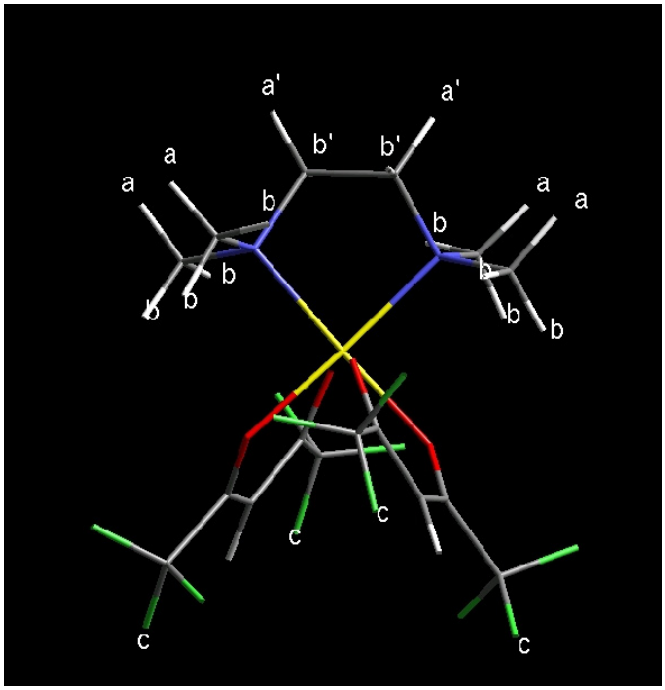

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Figure S2. U-B3LYP/TD-DFT/GTO energy levels of the frontier MOs for $Cu(hfa)_2$•TMEDA: (a) α- and β- MOs energies (C_2 optimized structure; 0 K) (b) α- and β- electronic Density of States (DOS) calculated on the structures sampled from the 397 K FPMD trajectory.

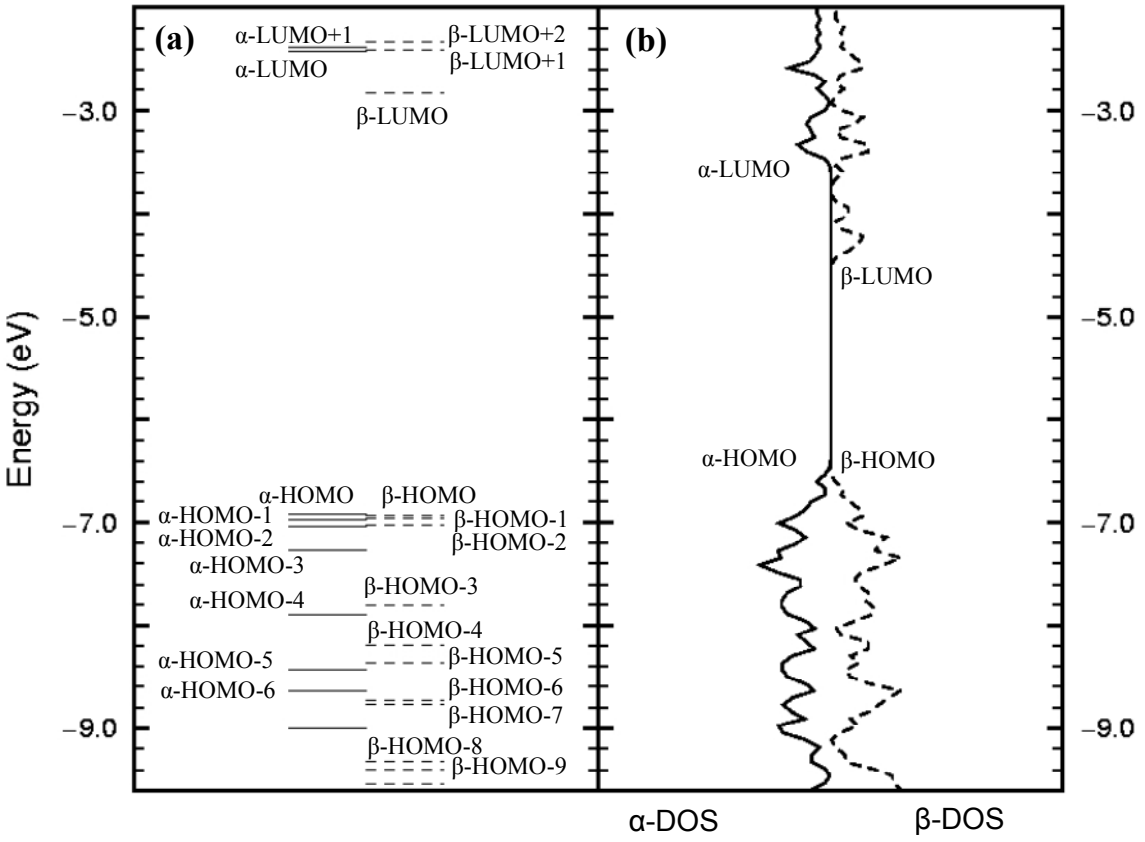

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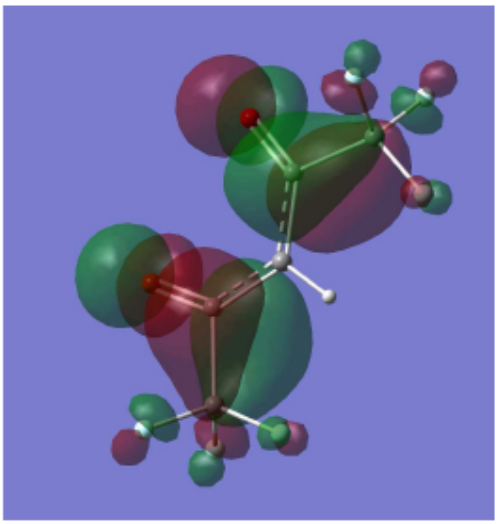
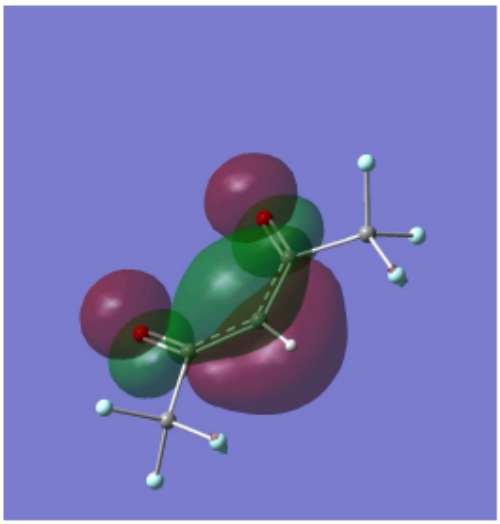
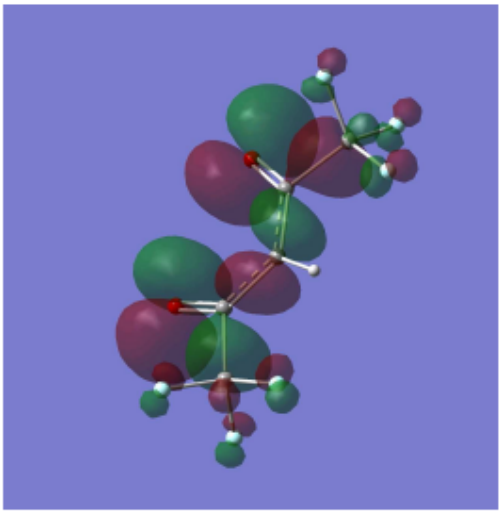
Figure S3. Representation of relevant molecular orbitals of isolated hfa.



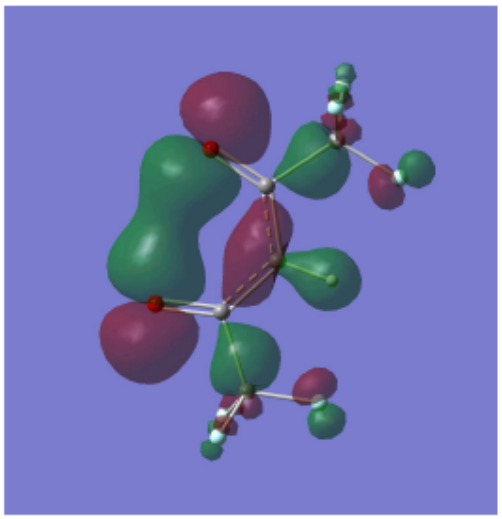
lumo (π* character)



homo (π character)



homo-1 (nσ character)



homo-2 (nσ character)

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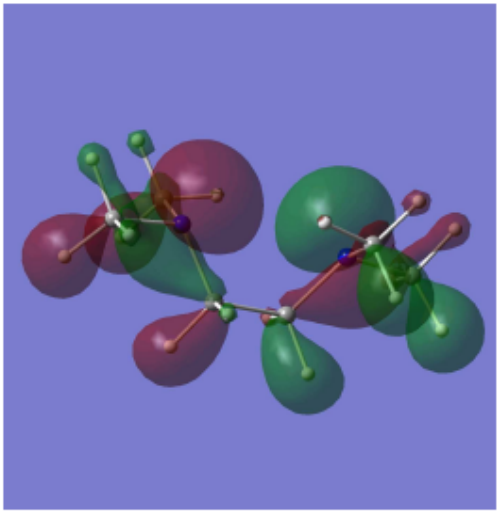
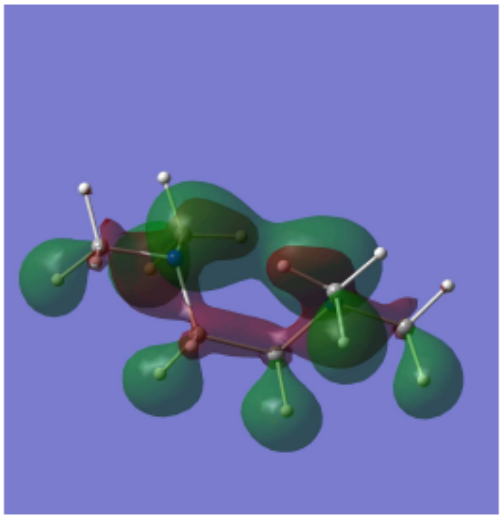
Figure S4. Representation of relevant molecular orbitals of isolated TMEDA.



homo (nσ character)



homo-1 (nσ character)

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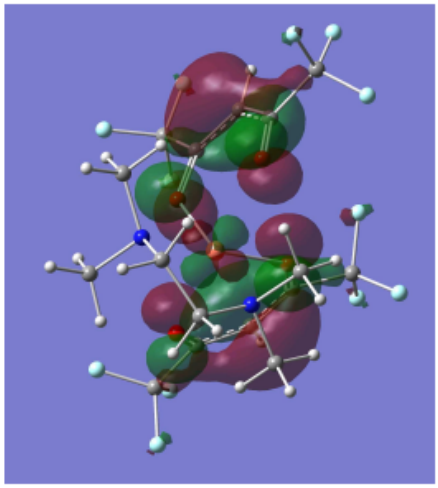
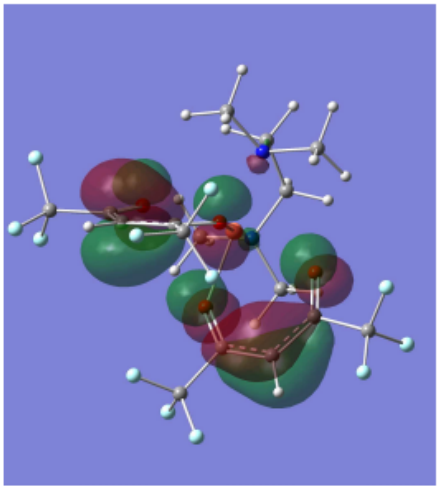
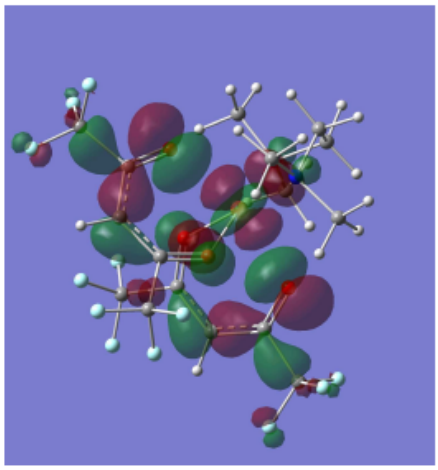
Figure S5 (a). Relevant occupied MOs of $Cu(hfa)_2$•TMEDA (β-spin).



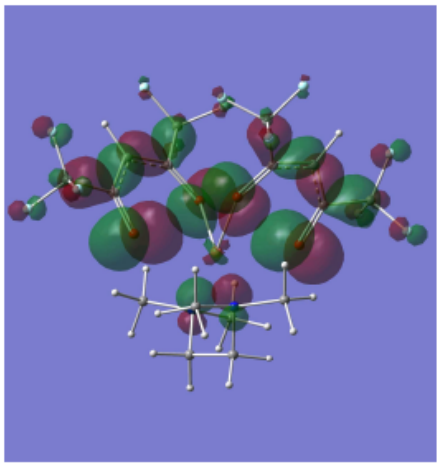
143β (β-HOMO): Combination Cu d_{yz}, hfa homo mainly localized on hfa (π character).



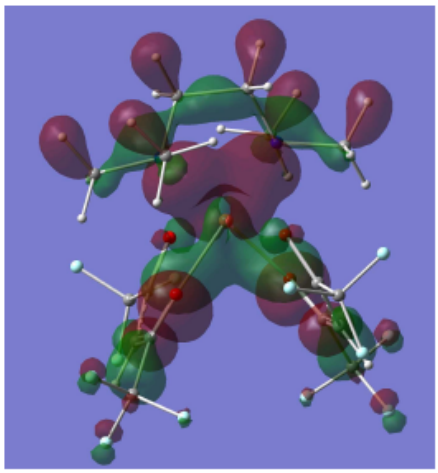
142β (β-HOMO-1): combination hfa homo (π character)



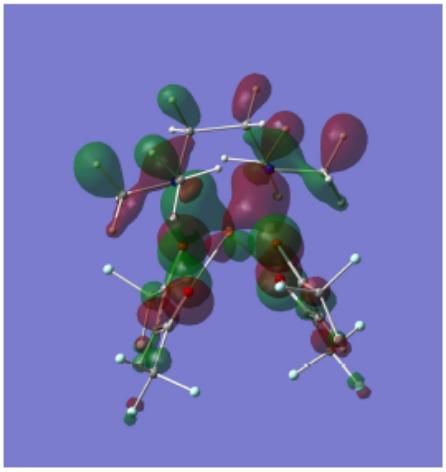
141β (β-HOMO-2): combination Cu d_z^2, hfa homo-1, TMEDA homo (mixed d-nσ character)



140β (β-HOMO-3): combination hfa homo-1 (nσ character) with minor contributions Cu d_{xz}, TMEDA homo



139β (β-HOMO-4) combination Cu d_z^2, hfa homo-2, TMEDA homo-1 (mixed d-nσ character)



138β (β-HOMO-5): combination Cu d_{xz}, TMEDA homo, hfa homo-2 (nσ character), mainly on ligands.

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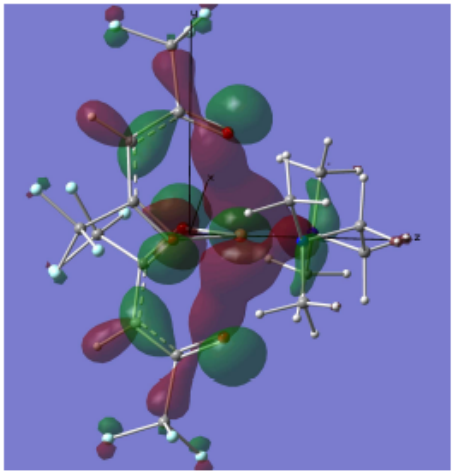
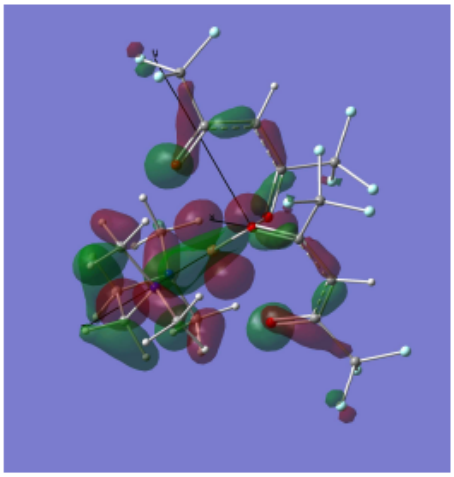
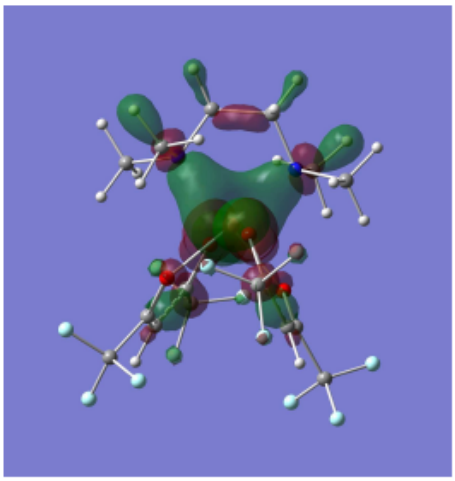


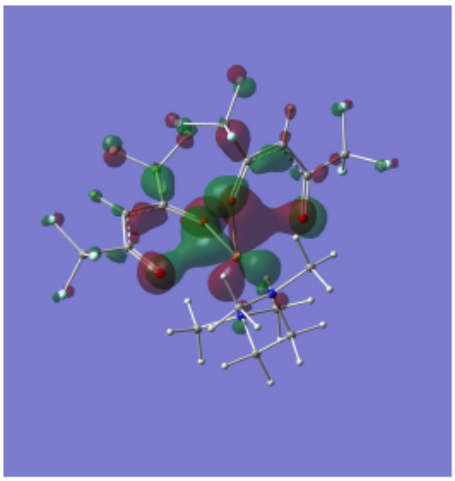
137β (β-HOMO-6): combination Cu d_{z^2}, hfa homo-2, TMEDA homo-1 with dominant d-metal character.



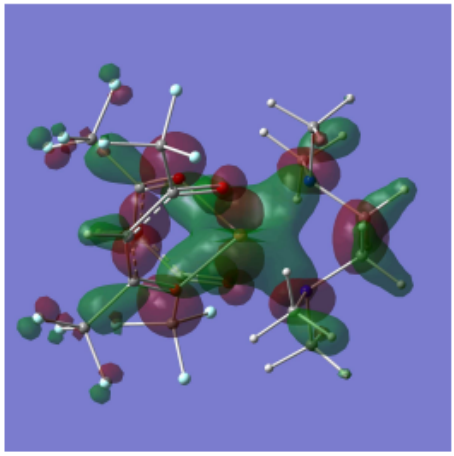
136β (β-HOMO-7): combination Cu d_{xy}, TMEDA homo, hfa homo-2 (mixed d-nσ character).



135β (β-HOMO-8): combination Cu d_{z^2}, hfa homo-2, TMEDA homo-1 with dominant d-metal character.



134β (β-HOMO-9): combination Cu d_{xz}, hfa homo-2 (Cu d-character).



133β (β-HOMO-10): combination Cu d_{yz}, TMEDA homo-1, hfa homo-2 (mixed d-nσ character).

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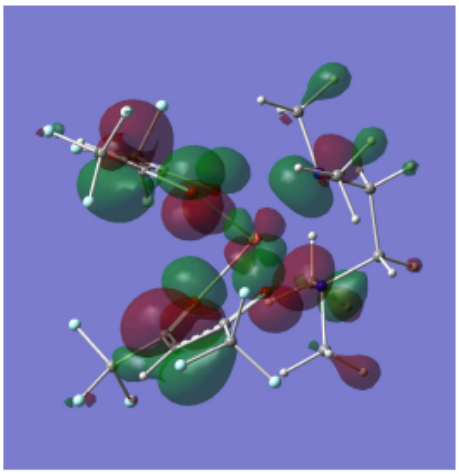
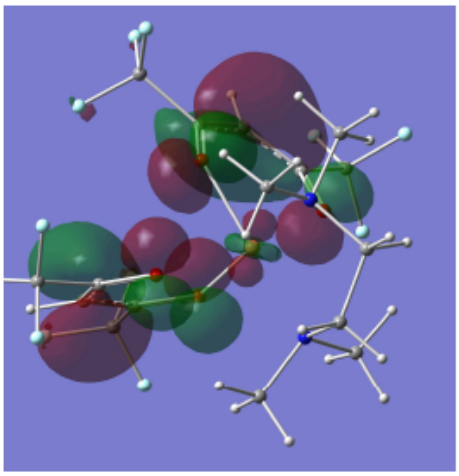
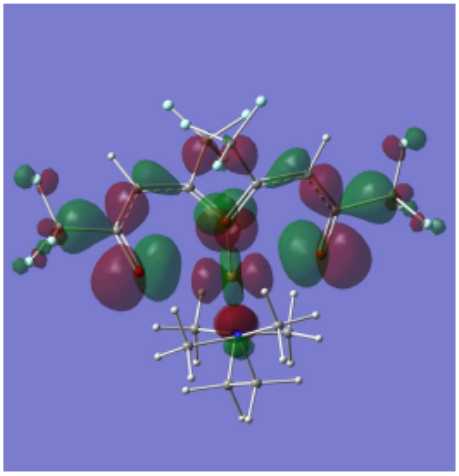
Figure S5 (b). Relevant occupied MOs of $Cu(hfa)_2$•TMEDA (α-spin).



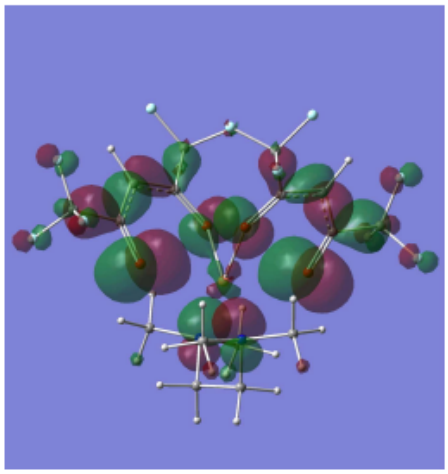
144α (α-HOMO): combination of Cu d_{xy}, hfa homo, TMEDA homo.



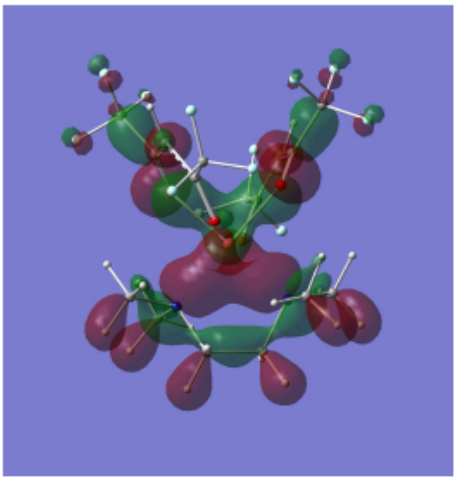
143α (α-HOMO-1): combination of hfa homo with minor Cu d_{z^2} contribution; dominant π character.



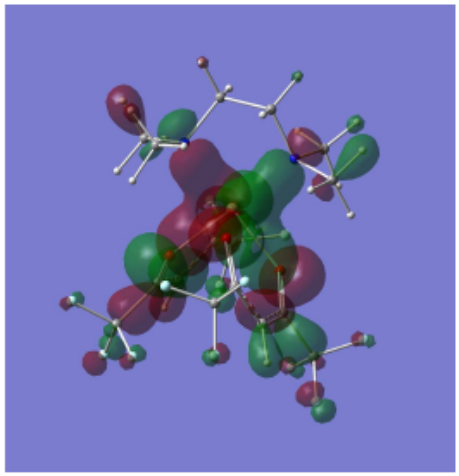
141α (α-HOMO-3): combination Cu d_{z^2}, hfa homo-1 (mixed d-nσ character)



140α (α-HOMO-4): combination hfa homo-1 (minor Cu d_{xz}, TMEDA homo contributions); dominant nσ character.



139α (α-HOMO-5): combination Cu d_{z^2}, hfa homo-2, TMEDA homo-1 (dominant nσ character).



138α (α-HOMO-6): combination hfa homo-2 (minor Cu d_{xz}, TMEDA homo contributions); dominant nσ character.

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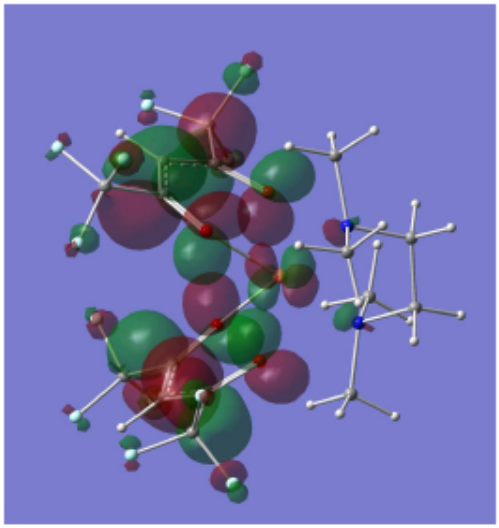
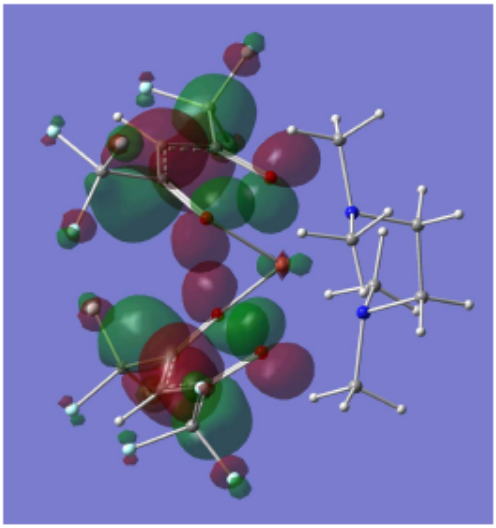
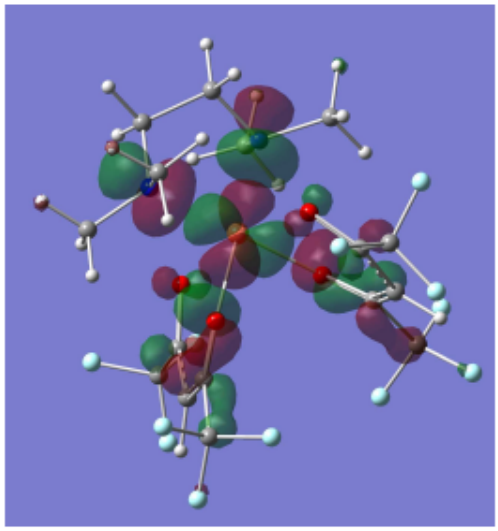
Figure S5 (c). Relevant empty MOs of $Cu(hfa)_2$•TMEDA (β-spin).



146β (β-LUMO+2): combination hfa lumo, Cu d_{xy}, mainly localized on hfa (dominant π* character).



145β (β-LUMO+1): combination hfa lumo (minor Cu $d_{x^2-y^2}$ contributions); dominant π* character.



144β (β-LUMO): combination Cu d_{xy}, hfa lumo, TMEDA homo with dominant Cu d-character.

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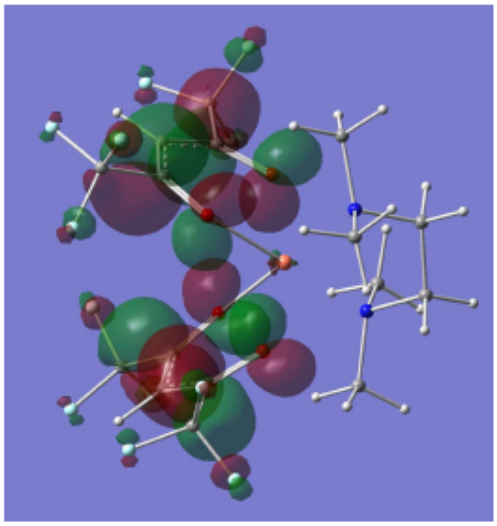
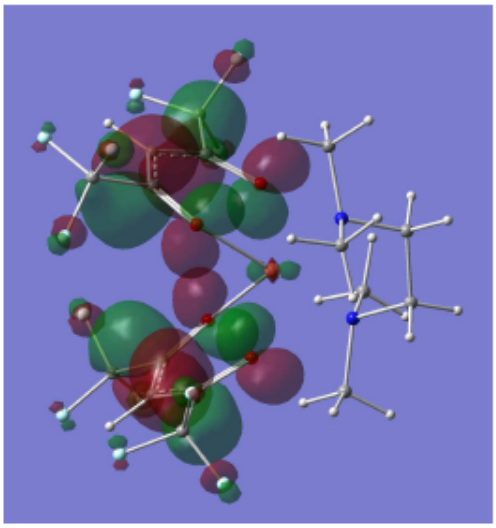
Figure S5 (d). Relevant empty MOs of $Cu(hfa)_2$•TMEDA (α-spin).



146α (α-LUMO+1): combination hfa lumo (π* character).



145α (α-LUMO): combination hfa lumo (minor Cu $d_{x^2-y^2}$ contribution); π* character.