Supplementary Information

Towards optimized photoluminescent Copper(I) phenanthroline-functionalized complexes: Control of the photophysics by symmetry breaking and spin-orbit coupling

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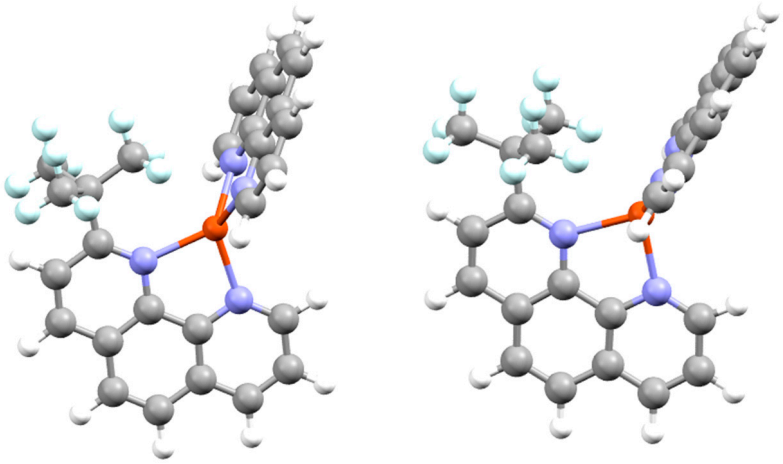


Figure *S*1: In (left) and out (right) orientations of a tBu group on a simplified complex holding only one tBu.

Structure	DEVVIJ[1]	DEVVIJ	BUFSOM[2]	BUZRIZ[3]	GATYUX[4]	MAHBOP[5]	NADGAA[6]	ELEZUS[7]	IBISOC[8]	$\mathbf{1_H}$
Cu-N	2.047	2.035	1.996	2.046	2.026	2.009	2.033	2.036	2.082	2.068
Cu-N	2.059	2.054	1.996	2.040	2.058	2.069	2.061	2.015	2.048	2.068
Cu-N	2.047	2.035	1.996	2.027	2.067	2.081	2.034	2.015	2.055	2.068
Cu-N	2.059	2.054	1.996	2.055	2.009	1.998	2.068	2.036	2.079	2.068
Cu-X_1	3.982	3.972	3.924	4.000	3.966	3.947	3.975	3.943	4.003	4.002
Cu-X_2	3.982	3.972	3.924	3.990	3.960	3.959	3.969	3.943	4.002	4.002
X_1-Cu-X_2	175.8	174.6	180.0	179.0	163.6	144.8	178.2	171.1	178.7	180.0
C_1-X_1-X_2-C_2	58.1	71.0	33.9	87.6	90.0	67.2	47.6	58.9	42.8	90.0

Table S1: Experimental (from CSD reference) and computed (GAUSSIAN) geometrical parameters for complex $\mathbf{1_H}$. Distances are in Angstroms, angles and dihedral angles in degrees.

Structure	DMPRCU[9]	DMPRCU	DMPNCU[10]	ABAFAN[11]	HEVPAA[12]	IPICUF[13]	NILHUL[14]	$\mathbf{1}_{Me}$
Cu-N	2.061	2.058	2.008	2.012	1.932	2.013	2.022	2.060
Cu-N	2.043	2.084	2.140	2.032	2.011	2.022	2.025	2.060
Cu-N	2.043	2.058	2.062	2.020	2.026	1.997	2.022	2.060
Cu-N	2.061	2.084	2.064	2.027	2.011	2.045	2.025	2.060
Cu-X_1	3.980	3.995	3.995	3.952	3.921	3.942	3.945	3.994
Cu-X_2	3.980	3.995	3.960	3.948	3.939	3.940	3.945	3.994
X_1-Cu-X_2	171.4	171.8	151.6	170.5	171.6	165.0	176.9	180.0
C_1-X_1-X_2-C_2	67.6	68.3	78.3	74.7	87.0	89.9	81.0	90.0

Table S2: Experimental (from CSD reference) and computed (GAUSSIAN) geometrical parameters for complex $\mathbf{1}_{Me}$**.** Distances are in Angstroms, angles and dihedral angles in degrees.

Structure	α	β	γ	δ	ζ	ε	2	3
Cu-N	2.075	2.141	2.113	2.129	2.144	2.144	2.155	2.035
Cu-N	2.075	2.141	2.133	2.161	2.144	2.146	2.155	2.290
Cu-N	2.075	2.142	2.120	2.129	2.147	2.181	2.169	2.114
Cu-N	2.075	2.142	2.121	2.161	2.147	2.114	2.169	2.114
Cu-X_1	3.931	4.032	3.998	4.033	4.037	4.036	4.081	4.095
Cu-X_2	3.931	4.035	4.005	4.033	4.041	4.042	4.083	4.028
X_1-Cu-X_2	180.0	180.0	172.4	172.4	180.0	178.2	180.0	176.4
C_1-X_1-X_2-C_2	90.0	84.7	89.1	88.8	90.0	88.4	90.0	90.0

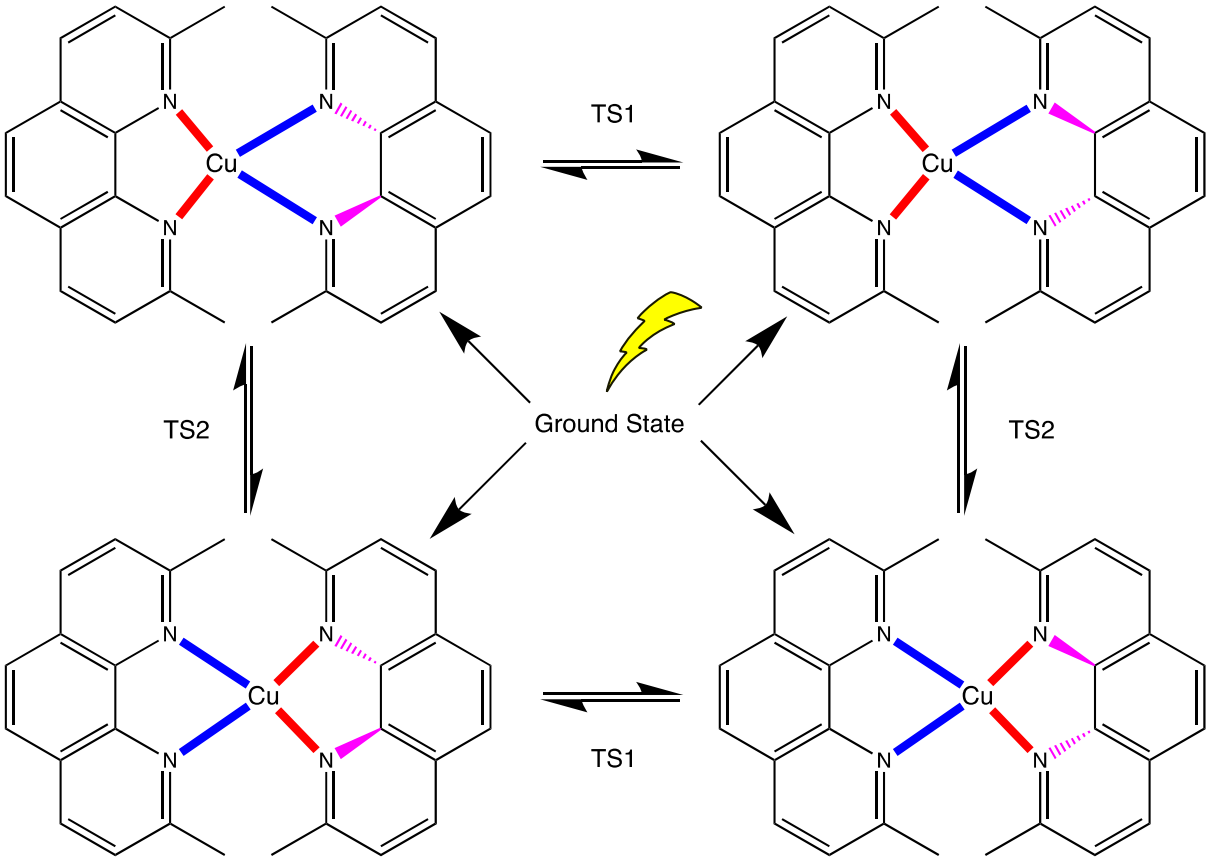
Table S3: Computed (GAUSSIAN) geometrical parameters for complexes $\mathbf{1}_{tBu}$**, 2** and **3** in the ground state. Distances are in Angstroms, angles and dihedral angles in degrees.

Structure	EDOFEJ[15]				
	δ	δ	δ	ζ	ε
Cu-N	2.103	2.076	2.081	2.105	2.072
Cu-N	2.120	2.139	2.105	2.108	2.145
Cu-N	2.096	2.096	2.092	2.104	2.148
Cu-N	2.129	2.115	2.114	2.111	2.079
Cu-X_1	3.992	3.984	3.976	4.005	4.002
Cu-X_2	3.999	3.997	3.980	3.990	4.000
X_1-Cu-X_2	174.6	170.2	176.6	177.0	176.0
C_1-X_1-X_2-C_2	81.2	89.6	88.5	86.6	85.7

Table S4: Experimental geometrical parameters for complex $\mathbf{1}_{tBu}$**.** Distances are in Angstroms, angles and dihedral angles in degrees.

Structure	1_H	1_H (TS1)	1_{Me}	1_{Me} (TS1)	1_{Me} (TS2)	1_{tBu}	1_{tBu} (TS2)	2	3
Cu-N	1.993	1.937	1.969	1.937	1.994	1.987	2.034	2.000	1.975
Cu-N	1.993	1.944	1.969	1.939	1.994	2.000	2.073	2.000	1.975
Cu-N	1.993	2.118	2.027	2.109	1.994	2.129	2.034	2.219	2.093
Cu-N	1.993	2.118	2.027	2.109	1.994	2.231	2.073	2.219	2.345
Cu-X_1	3.934	3.881	3.906	3.879	3.927	3.897	3.948	3.914	3.900
Cu-X_2	3.934	4.063	3.955	4.050	3.927	4.084	3.948	4.164	4.167
X_1-Cu-X_2	180.0	161.1	180.0	179.1	180.0	168.8	176.1	180.0	176.7
C_1-X_1-X_2-C_2	41.5	90.0	65.0	90.0	62.8	86.3	82.9	90.0	90.0
ΔG	0.0	12.9	0.0	4.4	-0.4	0.0	2.4		

Table S5: Computed (GAUSSIAN) geometrical parameters for complexes in the triplet state. The values are given for conformer δ for $\mathbf{1}_{tBu}$. Distances are in Angstroms, angles and dihedral angles in degrees and energies in kcal mol^{-1}.



Scheme S1: Representation of the four possible Triplet minima after irradiation of $\mathbf{1}_{Me}$ complex. In bold blue are the long Cu-N distance, in bold red the short Cu-N distance and in purple the indication of how the phen ligands is out of plane.

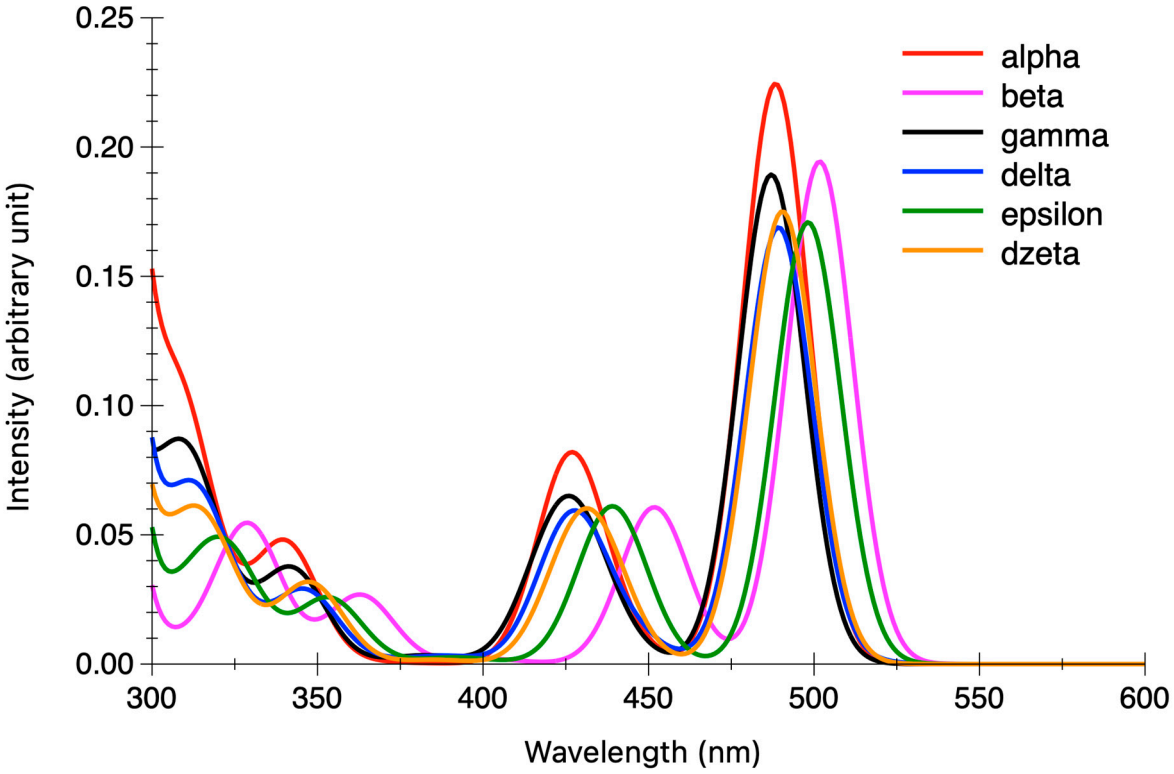


Figure S2: ADF computed Absorption spectra for the different conformers of $\mathbf{1}_{tBu}$.

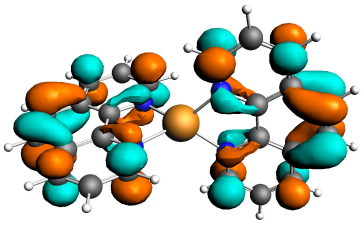
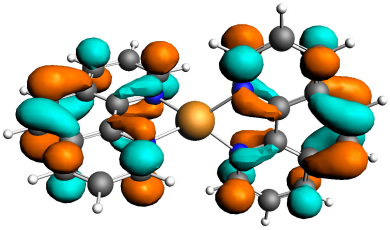
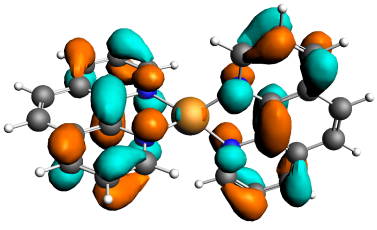
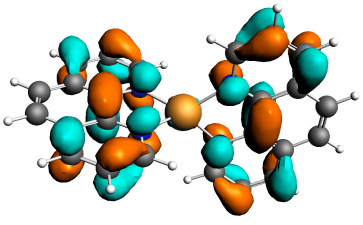
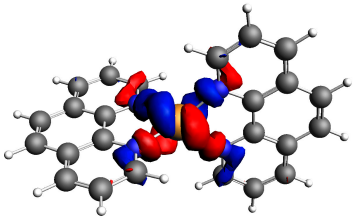
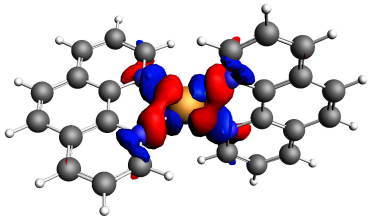
	
LUMO+2, -2.281	LUMO+3, -2.279
	
LUMO, -2.412	LUMO+1, -2.412
	
HOMO-1, -5.754	HOMO, -5.754

Figure S3: Frontier orbitals of $\mathbf{1}_{H}$ and energies in eV.

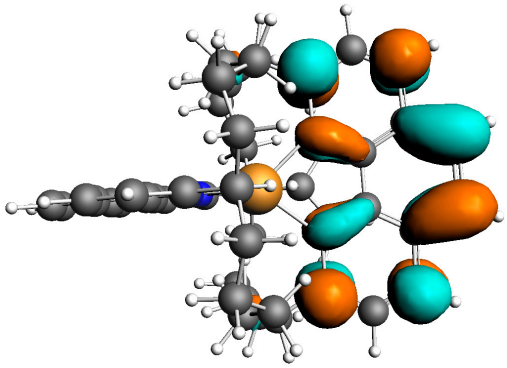
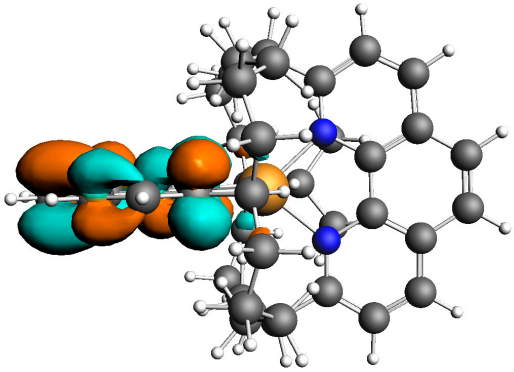
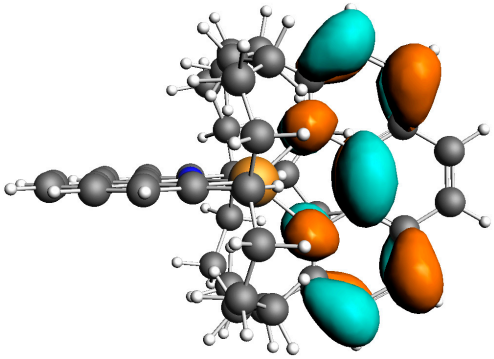
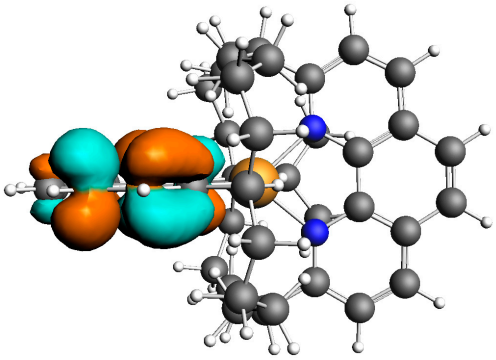
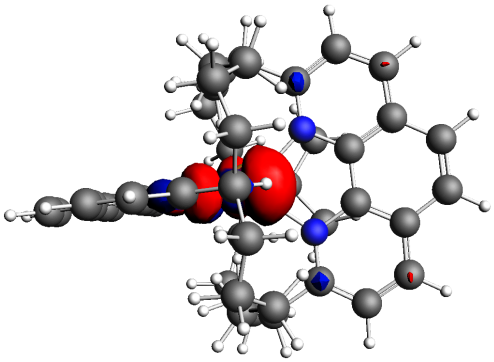
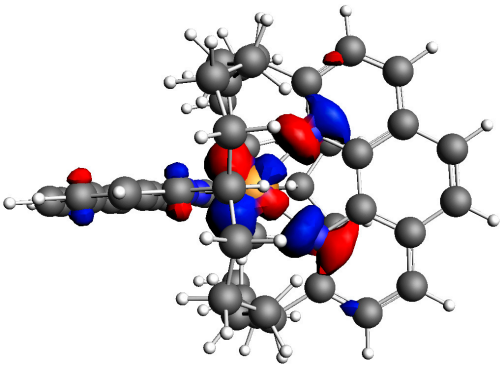
	
LUMO+2, -2.227	LUMO+3, -2.133
	
LUMO, -2.476	LUMO+1, -2.359
	
HOMO-1, -5.899	HOMO, -5.825

Figure S4: Frontier orbitals of **3** and energies in eV.

	S0 (D2d)	S1	T1	T2
Cu-N	2.062	2.004	1.991	2.028
	2.062	2.004	1.991	2.028
	2.062	2.064	2.035	2.028
	2.062	2.064	2.035	2.028
Cu-X_1	3.989	3.933	3.931	3.957
Cu-X_2	3.989	3.993	3.962	3.957

X_1-Cu-X_2	180.0	179.9	179.9	180.0
C_1-X_1-X_2-C_2	90.0	39.9	39.9	40.4

Table S6: Selected nuclear coordinates at the optimized ground state and low-lying excited states for **1H** computed with ADF. Distances are in Angstroms, angles and dihedral angles in degrees.

	S0 (D2d)	S1	T1	T2
Cu-N	2.056	1.985	1.990	2.019
	2.056	1.985	1.990	2.019
	2.056	2.102	2.047	2.020
	2.056	2.102	2.047	2.020
Cu-X_1	3.980	3.900	3.922	3.940
Cu-X_2	3.980	4.027	3.965	3.940
X_1-Cu-X_2	180.0	180.0	180.0	180.0
C_1-X_1-X_2-C_2	90.0	68.2	65.0	68.1

Table S7: Selected nuclear coordinates at the optimized ground state and low-lying excited states for **1Me** computed with ADF. Distances are in Angstroms, angles and dihedral angles in degrees.

	S0 (C2)	S1	T1	T2
Cu-N	2.118	2.005	1.996	2.035
	2.153	2.022	2.021	2.158
	2.118	2.171	2.168	2.032
	2.153	2.306	2.298	2.161
Cu-X_1	4.017	3.898	3.900	3.987
Cu-X_2	4.017	4.142	4.134	3.988
X_1-Cu-X_2	172.5	167.9	167.6	166.6
C_1-X_1-X_2-C_2	89.1	88.1	86.0	83.0

Table S8: Selected nuclear coordinates at the optimized ground state and low-lying excited states for **1tBu** for experimental δ structure computed with ADF. Distances are in Angstroms, angles and dihedral angles in degrees.

Structure	**1H**	**1Me**	**1tBu (α)**	**1tBu (β)**	**1tBu (γ)**	**1tBu (δ)**	**1tBu (ε)**	**1tBu (ζ)**	**2**	**3**
Cu-N	2.062	2.056	2.064	2.129	2.107	2.118	2.134	2.136	2.156	2.102
Cu-N	2.062	2.056	2.074	2.135	2.115	2.153	2.137	2.141	2.156	2.116
Cu-N	2.062	2.056	2.064	2.129	2.107	2.118	2.182	2.132	2.140	2.020
Cu-N	2.062	2.056	2.074	2.135	2.118	2.153	2.102	2.137	2.140	2.299
Cu-X_1	3.989	3.980	3.919	4.019	3.981	4.017	4.023	4.025	4.061	4.018
Cu-X_2	3.989	3.980	3.919	4.019	3.988	4.017	4.030	4.021	4.059	4.083
X_1-Cu-X_2	180.0	180.0	179.7	179.7	173.1	172.5	179.4	179.9	180.0	174.4
C_1-X_1-X_2-C_2	90.0	90.0	89.6	89.3	89.5	89.1	89.6	89.3	90.0	89.7

Table S9: Computed ground state (ADF) geometrical parameters. Distances are in Angstroms, angles and dihedral angles in degrees.

State	Conformer	α	β	γ	γ¹	δ	ε	ε¹	ζ	ζ¹
S1	Cu-N	1.980	2.022	1.996	2.189	2.005	2.016	2.215	2.018	2.223
	Cu-N	1.980	2.022	2.000	2.209	2.022	2.018	2.257	2.018	2.223
	Cu-N	2.139	2.239	2.145	2.002	2.171	2.229	2.017	2.222	2.01
	Cu-N	2.139	2.239	2.281	2.014	2.306	2.255	2.018	2.222	2.01
	Cu-X_1	3.839	3.908	3.873	4.082	3.898	3.901	4.139	3.908	4.126
	Cu-X_2	3.998	4.144	4.105	3.887	4.142	4.149	3.906	4.121	3.892
	X_1-Cu-X_2	180.0	180.0	169.4	170.6	167.9	176.3	179.1	180.0	180.0
	C_1-X_1-X_2-C_2	89.0	88.8	88.7	89.4	88.1	90.0	89.7	89.9	89.8
T1	Cu-N	1.985	2.015	1.989	2.165	1.996	2.008	2.210	2.010	2.220
	Cu-N	1.985	2.015	1.993	2.225	2.021	2.009	2.259	2.010	2.220
	Cu-N	2.108	2.237	2.154	2.012	2.168	2.221	2.008	2.220	2.003
	Cu-N	2.108	2.237	2.256	1.990	2.298	2.263	2.011	2.220	2.003
	Cu-X_1	3.853	3.908	3.873	4.077	3.900	3.899	4.136	3.907	4.122
	Cu-X_2	3.963	4.140	4.097	3.888	4.134	4.142	3.904	4.117	3.891
	X_1-Cu-X_2	180.0	180.0	170.4	170.1	167.6	175.8	179.2	180.0	180.0
	C_1-X_1-X_2-C_2	87.1	89.0	89.4	88.4	86.0	89.1	89.6	89.9	89.9

Table S10: Selected nuclear coordinates at the low-lying excited states for **1**$_{tBu}$ computed with ADF. Distances are in Angstroms, and angles in degrees.

State	Conformer	α	β	γ	γ¹	δ	ε	ε¹	ζ	ζ¹
	GS Symmetry	D_{2d}	D_{2d}	C_1	C_1	C_2	C_1	C_1	C_{2v}	C_{2v}
	S1 Symmetry	C_2	C_2	C_1	C_1	C_1	C_1	C_1	C_2	C_2
	E_{def}	0.542	0.497	0.279	0.287	0.286	0.376	0.374	0.249	0.244
	E_{em}	1.944	1.779	1.870	1.897	1.813	1.801	1.826	1.884	1.863
S1	E_{stab}	2.486	2.275	2.149	2.184	2.099	2.177	2.200	2.133	2.106
	ΔE	0.387	0.176	0.050	0.085	0.000	0.078	0.101	0.033	0.007
	λ_{em}	638	697	663	653	684	688	679	658	666
	f_{osc}	$1.06\ 10^{-5}$	$1.57\ 10^{-6}$	$1.53\ 10^{-5}$	$1.16\ 10^{-4}$	$2.54\ 10^{-4}$	$2.53\ 10^{-5}$	$2.20\ 10^{-7}$	$1.59\ 10^{-8}$	$1.07\ 10^{-7}$
	T1 Symmetry	C_2	C_2	C_1	C_1	C_1	C_1	C_1	C_2	C_2
	E_{def}	0.585	0.513	0.295	0.314	0.341	0.397	0.397	0.270	0.263
	E_{em}	1.745	1.633	1.715	1.731	1.656	1.648	1.671	1.726	1.707
	E_{stab}	2.331	2.146	2.011	2.044	1.997	2.046	2.068	1.997	1.970
	ΔE	0.360	0.175	0.040	0.074	0.027	0.075	0.098	0.026	0.000
T1	λ_{em}	710	759	723	716	749	752	742	718	726
	ΔE_{ST}	0.188	0.133	0.144	0.147	0.143	0.138	0.136	0.140	0.141
	SOC S1-T1	73.0	6.0	3.6	19.7	20.1	8.3	0.64	0.0	1.0
		$3.04\ 10^{-6}$	$2.10\ 10^{-9}$	$7.05\ 10^{-7}$	$7.42\ 10^{-6}$	$6.85\ 10^{-6}$	$4.25\ 10^{-6}$	$3.93\ 10^{-6}$	$1.09\ 10^{-13}$	$2.92\ 10^{-10}$
	f_{osc}	$8.97\ 10^{-6}$	$6.86\ 10^{-6}$	$4.69\ 10^{-5}$	$1.43\ 10^{-5}$	$2.77\ 10^{-5}$	$1.42\ 10^{-5}$	$2.04\ 10^{-4}$	$6.25\ 10^{-6}$	$7.43\ 10^{-6}$
		$3.04\ 10^{-4}$	$3.01\ 10^{-4}$	$2.81\ 10^{-4}$	$2.52\ 10^{-4}$	$1.77\ 10^{-04}$	$2.46\ 10^{-4}$	$3.98\ 10^{-5}$	$2.88\ 10^{-4}$	$3.77\ 10^{-4}$

Table S11: Emission data computed with ADF for S1 and T1 states of **1**$_{tBu}$. E_{def}, E_{em}, E_{stab}, ΔE and ΔE_{ST} are in eV, λ_{em} is in nm, SOC is in cm^{-1}. 1) Values for the 2nd minima due to oscillation of the exciton for γ, ε and ζ. Data are not given for α, β and δ because the second minima is strictly identical to the first one due to symmetry.

	S1	S2	S3	S4	T1	T2	T3	T4
T1	0.0	0.0	302.0	6.8	0.0	0.0	0.0	381.0
T2	269.0	0.0	0.0	21.6	0.0	0.0	421.1	0.0
T3	0.0	0.0	0.0	18.7	0.0	421.1	0.0	0.0
T4	0.0	295.8	0.0	10.3	381.1	0.0	0.0	0.0

Table S12: Spin-orbit coupling (in cm^{-1}) between the low-lying excited states in **1**$_{Me}$ computed with ADF.

	Structure	2	2	3	3
S1	Cu-N	2.017	2.271	1.989	2.200
	Cu-N	2.017	2.271	1.996	2.209
	Cu-N	2.254	2.017	2.122	1.980
	Cu-N	2.254	2.017	2.364	1.999
	Cu-X_1	3.910	4.193	3.899	4.132
	Cu-X_2	4.194	3.932	4.182	3.906
	X_1-Cu-X_2	180.0	180.0	174.9	176.5
	C_1-X_1-X_2-C_2	90.0	90.0	89.3	89.7
T1	Cu-N	2.010	2.269	1.978	2.205
	Cu-N	2.010	2.269	1.995	2.193
	Cu-N	2.250	2.011	2.120	1.973
	Cu-N	2.250	2.011	2.354	1.988
	Cu-X_1	3.908	4.192	3.899	4.125
	Cu-X_2	4.189	3.933	4.177	3.903
	X_1-Cu-X_2	180.0	180.0	175.1	176.5
	C_1-X_1-X_2-C_2	90.0	89.7	88.9	89.8

Table S13: Computed S1 and T1 (ADF) geometrical parameters. Distances are in Angstroms, angles and dihedral angles in degrees.

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