

Restricted Photochemistry in the Molecular Solid State: Structural changes on Photoexcitation of Cu(I) Phenanthroline metal-to-ligand-charge-transfer (MLCT) complexes by Time-Resolved Diffraction

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Supplementary Material

Refinement strategy with the program LASER2010.

Refinements were performed separately for each of the two sets of temperatures. The six data sets listed in Table S1 were used in each case. Only data with $|h|/\sigma(\eta) > 1$ were used in the refinement giving a total of 12209 and 4260 independent reflections for the 90K and 180K datasets respectively.

Both refinements followed the same strategy.

The ground-state Cu positions were taken as starting points in the ES refinement. Initial cycles included only the excited state positions of the atoms for which definitive features in the photodifference maps were observed i.e. the copper and phosphorus atoms, followed by refinement of the excited state populations and k_B parameters. Subsequent refinements employed a rigid body model. Each of the ligands of the Cu atoms in the excited state was treated as a separate rigid body.

The GS and ES Cu atoms, ES P atoms and GS B atoms were allowed to refine as independent atoms. The phenanthroline ligands were anchored to the ES copper atoms to which they were bound. They were allowed to pivot around their anchor position, translate as the ES copper positions, and additionally to translate along the direction connecting the corresponding ES Cu atom with the midpoint of the N atoms from the ES phenanthroline, thus allowing for the Cu – N bond length adjustments. Each of the phosphine ligands was anchored to the corresponding phosphorus atom and therefore allowed to translate with it and pivot around it. Each of the two independent GS Cu(phen)(PPh₃)₂ cations was treated as a separate rigid body anchored to the metal atom and allowed to translate with it and pivot around it. Analogously the BF₄ anions were treated as separate rigid bodies anchored to the corresponding B atoms. The subsequent steps of the refinement included refining of the ES independent atoms positions, ES rigid bodies positions and rotations and the ES occupancies and k_B values. The positions and rotations of the GS moieties were also allowed to refine. Of the latter, only the rotations of the BF₄ anions were significant, in agreement with the tendency of this moiety to display dynamical disorder and rotate relatively freely inside their almost spherical crystal lattice cavities. A total of 74 parameters were refined, including the 30 positional parameters of 10 independent atoms (all of these being simultaneously anchor atoms to the connected rigid bodies), 30 rotational parameters, 3 per rigid body, 2 additional translation of the ES phenanthrolines and 6 temperature scale factors k_B and 6 independent ES

occupancy parameters.

Table S1. Crystal size, applied laser power, number of raw and merged data, R merge and completeness to 0.52 Å for all crystal samples. Only reflections for which signal was registered on all 10 ON/OFF frames were included.

	Laser mJ/mm ² /pulse	Crystal size um	phi scan range °	#	R _{merge}	#merged	%
180K							
180-1	0.9	15x40x100	0-90	25463	0.024	5608	55.1
180-2	1.1	15x40x100	0-90	12563	0.024	4989	49.9
180-3	0.7	25x50x80	0-90	9125	0.026	4096	40.6
180-4	0.8	25x50x80	0-90	8609	0.026	3936	39.2
180-5	0.6	10x40x80	0-90	2807	0.036	1343	13.0
180-6	0.7	10x40x80	0-30	3167	0.298	1926	19.3
90K							
90-1	1.6	30x40x50	0-90	10091	0.034	3010	30.9
90-2	1.6	20x50x100	0-90	14520	0.029	4283	42.8
90-3	1.6	30x70x75	0-90	16955	0.032	4556	45.4
90-4	1.6	20x40x80	0-90	15467	0.033	4138	41.7
90-5	1.6	25x50x80	0-90	10813	0.035	3249	32.5
90-6	1.6	25x60x70	0-90	21189	0.027	5157	51.5

Table S2. (a) Crystallographic information on GS structures from the monochromatic experiments and (b) Geometrical parameters of the compound (**2**) in the excited state. Top:180K; Lower: 90K.

(a)

cell measurement temperature	90(2)	180(2)
X-ray radiation wavelength	0.71	
chemical formula moiety	'C48 H38 Cu N2 P2, B F4'	
symmetry cell setting	triclinic	
symmetry space group name H-M	P-1	
a / Å	17.3560(12)	17.4719(15)
b / Å	19.2626(13)	19.3926(17)
c / Å	12.7731(9)	12.8340(11)
alpha / °	80.452(2)	80.579(2)
beta / °	84.386(2)	84.560(2)
gamma / °	106.019(2)	106.466(2)
volume / Å ³	4000.9(5)	4067.8(6)
formula units Z	4	4
crystal size max / mm	0.22	0.17
crystal size mid / mm	0.1	0.11

crystal size min / mm	0.09	0.08
crystal density / gcm ⁻³	1.42	1.4
crystal F 000	1760	1760
absorpt coefficient mu / mm ⁻¹	0.68	0.67
reflns number	19913	27328
Rmerge	0	0
theta max / °	28.34	31.69
reflns number gt>2sigma(I)	13137	13808
ls number parameters	1045	1045
R	0.04	0.05
wR	0.1	0.15
Goof	0.94	0.98
fraction theta max / %	1	0.99
diff density max / eÅ ⁻³	0.62	1.1
diff density min / eÅ ⁻³	-0.48	-0.73
diff density rms / eÅ ⁻³	0.08	0.08

(b)

ES bond lengths			
angles (Å, °)			
Cu(1)-P(1)	2.329(12)	Cu(1)-P(2)	2.230(16)
	2.228(5)		2.250(7)
Cu(2)-P(3)	2.221(14)	Cu(2)-P(4)	2.273(14)
	2.248(2)		2.267(6)
Cu(1)-N(1)	2.056(9)	Cu(1)-N(2)	2.114(9)
	2.064(5)		2.121(5)
Cu(2)-N(3)	2.039(8)	Cu(2)-N(4)	2.038(7)
	2.030(6)		2.027(6)
P(2)-Cu(1)-P(1)	124.165(8)	P(3)-Cu(2)-P(4)	121.682(9)
	124.837(3)		123.262(4)
N(1)-Cu(1)-N(2)	82.103(7)	N(3)-Cu(2)-N(4)	82.371(13)
	81.659(3)		82.747(4)

Table S3. Final agreement factors after LASER2010 refinements. Datasets were not merged for the LASER refinements, hence total number of the reflections is larger than that reported for the photodifference maps. Top: 180K; Lower: 90K.

	# η /s(η) > 1	R(η)	wR(η)	<η>_obs	< η >_obs	R(R)	Goof
180-1	1148	0.522	0.593	-0.026	0.044	0.024	0.815

180-2	577	0.598	0.653	-0.028	0.047	0.029	0.795
180-3	1322	0.392	0.427	-0.053	0.064	0.026	0.617
180-4	745	0.478	0.533	-0.042	0.054	0.027	0.777
180-5	238	0.514	0.506	-0.046	0.064	0.034	0.850
180-6	230	0.523	0.530	-0.066	0.072	0.040	0.622
180K all	4260	0.476	0.521	-0.040	0.055	0.033	0.862
90-1	1635	0.382	0.411	-0.085	0.092	0.039	1.005
90-2	2058	0.373	0.408	-0.061	0.072	0.029	0.833
90-3	2396	0.395	0.435	-0.062	0.073	0.031	1.047
90-4	2527	0.370	0.395	-0.084	0.092	0.037	1.027
90-5	1508	0.438	0.460	-0.071	0.082	0.038	0.983
90-6	2085	0.433	0.474	-0.043	0.059	0.027	0.841
90K all	12209	0.394	0.425	-0.068	0.078	0.033	0.981

Table S4. Changes of Cu coordination sphere angles on excitation, Δ =ES-GS. U indicates UFF force-field used in QM/MM approach while C indicates embedded charge, utilized in QM/MM according to description in the paper.

compound	atom	T(K)	rocking			wagging			flattening		
			GS	ES	Δ	GS	ES	Δ	GS	ES	Δ
Cu bis(tppp) (2) This study	Cu(1)	90	75.2	75.6	0.3(3)	91.4	91.4	0.0(3)	97.3	98.1	0.9(3)
		180	75.2	74.1	-1.0(6)	90.7	93.6	2.8(7)	96.6	99.7	3.1(6)
	Cu(2)	90	88.7	89.6	0.9(3)	95.3	94.3	-1.0(4)	96.9	99.7	2.7(2)
		180	88.9	90.2	1.4(7)	94.7	93.1	-1.6(8)	96.8	101.2	4.4(5)
Cu(dmp)(dppe) 2009	Cu(1)	16	95.6	90.4	-5.2(5)	84.1	85.1	1.0(5)	92.8	92.7	-0.1
	Cu(2)			86.5	-4.9(5)		88.6	-6.7(5)	90.5	93.7	3.2
Cu bis(tppp) nitrate. ²⁸	Cu	133	85.3	-	-	89.0	-	-	77.5	-	-
Cu bis(tpp(dmp)) nitrate. ²⁸	Cu	294	85.5	-	-	87.1	-	-	95.8	-	-
Theory isolated molecule 6-31G*	Cu	-	90	86.7	3.3	86.3	90.7	4.4	92.2	123.5	31.3

Table S5. Pre-exponential factors (A) and lifetimes (τ) of the fits to the time-resolved emission measurements at different temperatures.

Temperature (K)	A_1	τ_1	A_2	τ_2
50	0.0613(2)	11.92(7)	0.14973(12)	115.53(9)
90	0.0467(2)	9.96(7)	0.14567(11)	102.15(7)
180	0.0262(2)	7.69(10)	0.14470(11)	71.79(5)

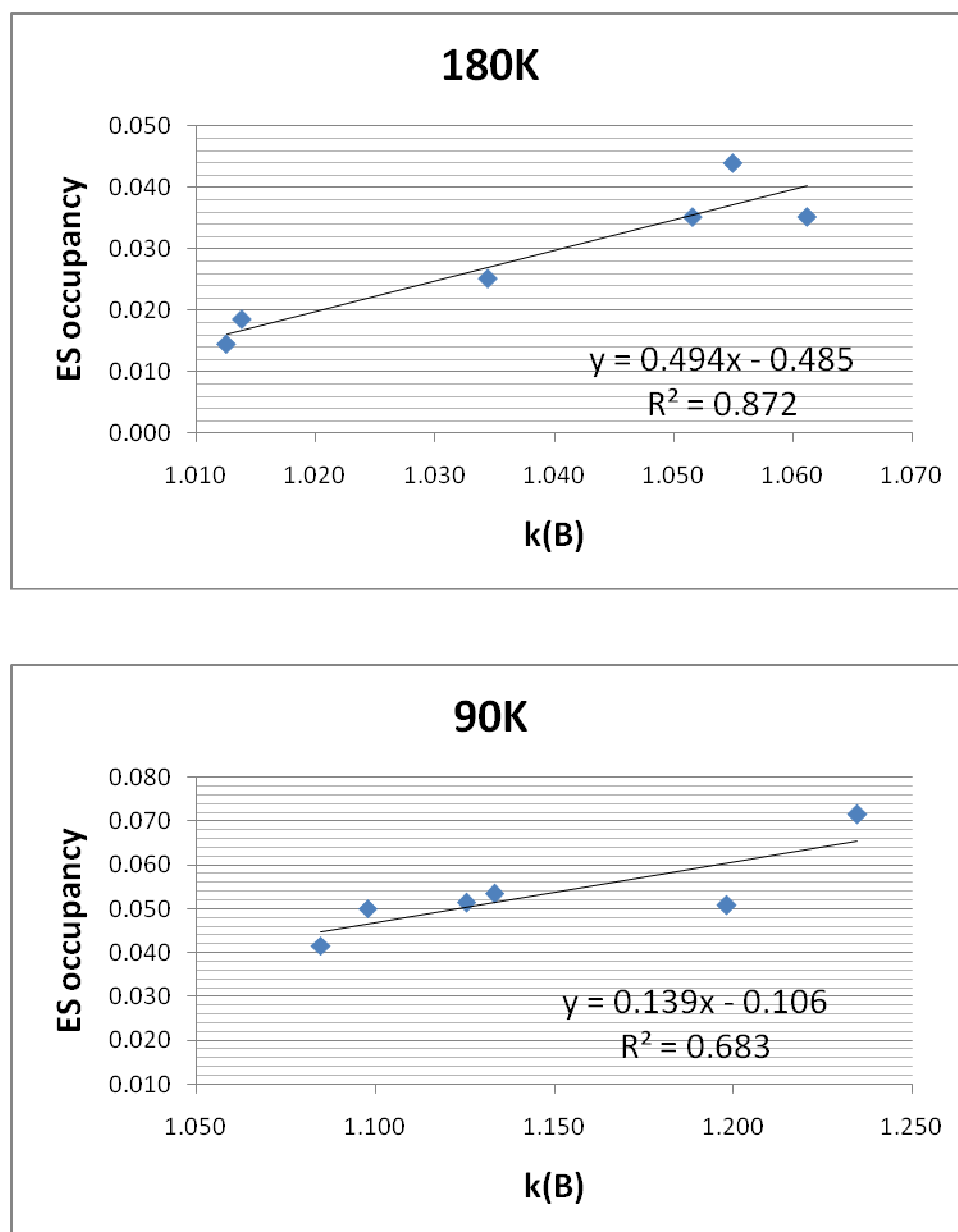


Fig. S1. Relation between the temperature scale factor and conversion percentage to the excited state for each of the six data sets collected at 180K (top) and 90K (lower)

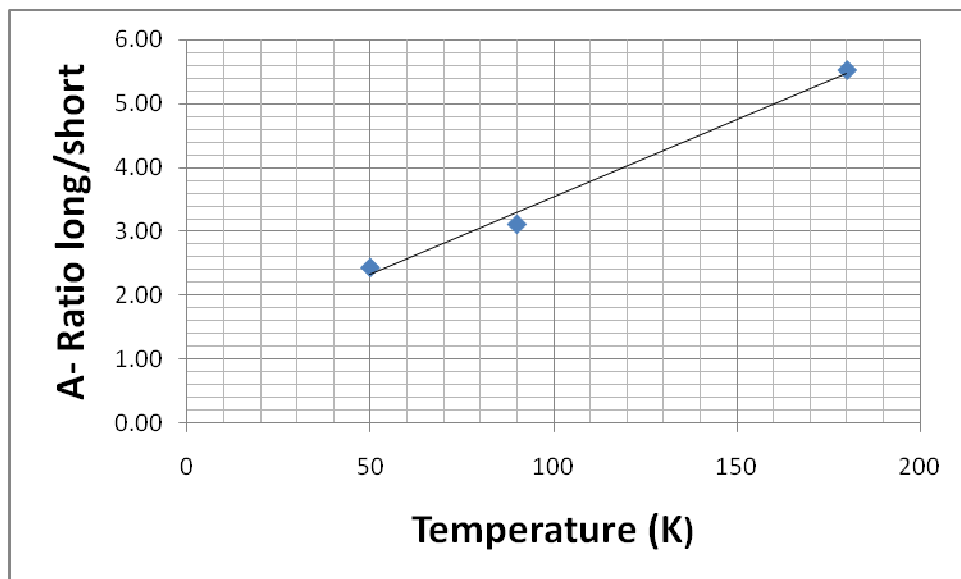


Fig. S2. Relation between the ratio of the pre-exponential factors of the long- and short-lifetime emissions and the temperature of measurement.