Supporting Information

for

A Theoretical Analysis of the Phosphorescence Efficiencies of Cu(I) Complexes

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Table S1. Molecular orbital compositions in S_0 States for these complexes (%)

	$[Cu(phen)(PPh_3)_2]^+$			$[Cu(dmp)(PPh_3)_2]^+$			$[Cu(dbp)(PPh_3)_2]^+$			$[Cu(phen)(POP)]^+$			$[Cu(dmp)(POP)]^+$			$[Cu(dbp)(POP)]^+$		
	Cu	PPh_3	NN	Cu	PPh_3	NN	Cu	PPh_3	NN	Cu	POP	NN	Cu	POP	NN	Cu	POP	NN
H-2	69.0	4.9	26.1	69.0	3.7	27.4	68.8	3.5	27.7	50.0	32.1	17.9	51.6	30.4	18.0	66.1	8.6	25.3
H-1	38.6	53.2	8.2	44.3	45.9	9.8	45.3	44.3	10.4	43.0	49.0	8.0	50.3	38.1	11.6	45.5	44.2	10.2
H	32.9	63.6	3.5	34.2	61.2	4.6	34.9	59.8	5.4	34.2	62.2	3.6	36.1	59.0	4.9	37.7	57.2	5.0
L	3.1	3.4	93.6	3.1	3.5	93.4	2.7	3.6	93.8	3.1	3.3	93.6	3.4	3.4	93.3	2.9	3.4	93.7
L+1	0.2	0.8	99.0	0.2	0.8	99.0	0.2	0.8	99.0	0.1	0.7	99.2	0.3	1.5	98.2	0.3	0.8	98.9
L+2	8.2	14.5	77.3	3.9	93.9	2.2	4.2	92.8	3.0	1.6	96.2	2.2	1.4	94.3	4.3	1.4	95.8	2.8

Table S2. Molecular orbital compositions of Cu at S_0 State in Solvent DCM ($c_d^2 > 1\%$)

	MO	Energy (eV)	Cu contribution (%)
[Cu(phen)(PPh_3)$_2$]$^+$	L	-2.32	3.46 (1.25 d_{xy})
	H	-6.13	35.74 (27.00 d_{xy})
	H-1	-6.47	43.67 (21.34 $d_{x^2-y^2}$ +13.47 d_{z^2})
[Cu(dmp)(PPh_3)$_2$]$^+$	L	-2.25	3.35 (1.15 d_{xy})
	H	-6.13	35.98(27.81 d_{xy})
	H-1	-6.45	47.71 (23.58 $d_{x^2-y^2}$ +15.10 d_{z^2})
[Cu(dbp)(PPh_3)$_2$]$^+$	L	-2.23	2.80
	H	-6.14	36.22 (18.50 d_{yz} +10.11 d_{xz})
	H-1	-6.46	47.85 (25.26 d_{xy} +8.95 $d_{x^2-y^2}$ +4.69 d_{z^2})
[Cu(phen)(POP)]$^+$	L	-2.30	3.48 (1.40 $d_{x^2-y^2}$)
	H	-5.99	37.03 (29.02 $d_{x^2-y^2}$)
	H-1	-6.45	48.26 (19.85 d_{xy} +17.87 d_{z^2} +1.94 d_{yz})
[Cu(dmp)(POP)]$^+$	L	-2.23	3.57 (1.08 $d_{x^2-y^2}$)
	H	-6.00	38.28 (31.36 $d_{x^2-y^2}$)
	H-1	-6.53	66.01 (34.30 d_{yz} +25.00 d_{xz} +3.40 d_{xy})
[Cu(dbp)(POP)]$^+$	L	-2.19	3.06
	H	-6.07	39.06 (21.37 d_{z^2} +5.20 $d_{x^2-y^2}$ +4.82 d_{yz} +1.44 d_{xy})
	H-1	-6.43	49.63 (21.41 d_{yz} +12.84 $d_{x^2-y^2}$ +4.48 d_{xy} +3.73 d_{xz})

Table S3. Emission Spectra Obtained by TDDFT Method for these Complexes, Together with Experimental Values

	Electronic transitions	λ^{em} (nm)	Excitation energies (eV)	Main configurations	
$[Cu(phen)(PPh_3)_2]^+$	$T_1 \rightarrow S_0$	834.4/680[a]	1.49	HOMO→LUMO	0.69
				HOMO-2→LUMO	0.11
$[Cu(dmp)(PPh_3)_2]^+$	$T_1 \rightarrow S_0$	607.1/560[a]	2.04	HOMO-2→LUMO	0.60
				HOMO→LUMO	-0.33
$[Cu(dbp)(PPh_3)_2]^+$	$T_1 \rightarrow S_0$	607.2	2.04	HOMO-2→LUMO	0.57
				HOMO→LUMO	-0.36
$[Cu(phen)(POP)]^+$	$T_1 \rightarrow S_0$	812.6/700[a]	1.53	HOMO→LUMO	0.69
$[Cu(dmp)(POP)]^+$	$T_1 \rightarrow S_0$	658.0/570[a]	1.88	HOMO→LUMO	0.68
$[Cu(dbp)(POP)]^+$	$T_1 \rightarrow S_0$	611.9/560[a]	2.03	HOMO-2→LUMO	0.50
				HOMO→LUMO	0.36

[a] Measured in DCM in reference [13].

Table S4. Molecular orbital compositions of Cu at T_1 State in Solvent DCM (c_d^2 >1%)

	MO	**Energy (eV)**	**Cu contribution (%)**
$\mathbf{[Cu(phen)(PPh_3)_2]^+}$	**L**	**-2.73**	**4.55 (1.98 d_{xy})**
	H	**-5.38**	**41.77 (28.09 d_{xy} +5.61 d_{yz} +3.06 $d_{x^2-y^2}$)**
	H-1	**-6.44**	**36.05 (11.15 d_{z^2} +8.63 $d_{x^2-y^2}$ +7.21 d_{xz})**
$\mathbf{[Cu(dmp)(PPh_3)_2]^+}$	**L+1**	**-2.19**	**4.00 (1.33 d_{xy})**
	H	**-6.08**	**32.23 (25.65 d_{xy})**
	H-1	**-6.45**	**6.39 (3.49 d_{xy})**
$\mathbf{[Cu(dbp)(PPh_3)_2]^+}$	**L+1**	**-2.16**	**3.32**
	H	**-6.08**	**31.21 (17.12 d_{yz} +8.10 d_{xz})**
	H-1	**-6.41**	**9.58 (3.82 d_{yz} +1.21 d_{xz})**
$\mathbf{[Cu(phen)(POP)]^+}$	**L**	**-2.64**	**4.86 (1.39 $d_{x^2-y^2}$)**
	H	**-5.34**	**42.64 (20.27 $d_{x^2-y^2}$ +12.60 d_{xy} +4.53 d_{yz} +1.88 d_{xz})**
	H-1	**-6.47**	**49.61 (30.82 d_{yz} +6.22 d_{z^2} +4.10 $d_{x^2-y^2}$ +2.05 d_{xy})**
$\mathbf{[Cu(dmp)(POP)]^+}$	**L**	**-2.59**	**4.44 (1.82 $d_{x^2-y^2}$)**

	H	**-5.57**	**42.59 (29.88 $d_{x^2-y^2}$ +6.97 d_{xz} +1.15 d_{yz})**
	H-1	**-6.32**	**59.75 (30.17 d_{yz} +19.80 d_{xz} +5.01 d_{xy})**
[Cu(dbp)(POP)]$^+$	**L**	**-2.44**	**3.86**
	H	**-6.02**	**34.38 (17.05 d_{z^2} +6.34 d_{yz} +5.73 $d_{x^2-y^2}$)**
	H-1	**-6.38**	**27.83 (11.36 d_{xz} +7.23 $d_{x^2-y^2}$ +2.59 d_{z^2} +1.99 d_{xy} +1.03 d_{yz})**

Table S5. SOC matrix elements between the $^3(\mathrm{d}_k\pi^*)$ and $^1(\mathrm{d}_l\pi^*)$ states.

	$^1(\mathrm{d}_{xz}\pi^*)$	$^1(\mathrm{d}_{yz}\pi^*)$	$^1(\mathrm{d}_{z^2}\pi^*)$	$^1(\mathrm{d}_{xy}\pi^*)$	$^1(\mathrm{d}_{x^2-y^2}\pi^*)$
$^3(\mathrm{d}_{xz}\pi^*)$	0	$\frac{c_{xz}c_{yz}}{2}$	$-\frac{\sqrt{3}}{2}c_{xz}c_{z^2}$	$-\frac{c_{xz}c_{xy}}{2}$	$-\frac{c_{xz}c_{x^2-y^2}}{2}$
$^3(\mathrm{d}_{yz}\pi^*)$	$-\frac{c_{yz}c_{xz}}{2}$	0	$-\frac{\sqrt{3}}{2}c_{yz}c_{z^2}$	$-\frac{c_{yz}c_{xy}}{2}$	$\frac{c_{yz}c_{x^2-y^2}}{2}$
$^3(\mathrm{d}_{z^2}\pi^*)$	$\frac{\sqrt{3}}{2}c_{z^2}c_{xz}$	$\frac{\sqrt{3}}{2}c_{z^2}c_{xz}$	0	0	0
$^3(\mathrm{d}_{xy}\pi^*)$	$\frac{c_{xy}c_{xz}}{2}$	$\frac{c_{xy}c_{yz}}{2}$	0	0	$-c_{xy}c_{x^2-y^2}$
$^3(\mathrm{d}_{x^2-y^2}\pi^*)$	$\frac{c_{x^2-y^2}c_{xz}}{2}$	$-\frac{c_{x^2-y^2}c_{yz}}{2}$	0	$c_{x^2-y^2}c_{xy}$	0

Table S6. Electronic transitions of phen-pop calculated at the T_1 optimized geometry by TDDFT in Solvent DCM (CI > 0.20)

S_n/T_m	**Excitation energies (eV)**	**λ (nm)**	**Energy (cm^{-1})**	***f***	**Main configurations**	
T_1	**1.66**	**746.4**	**13398**	**0.0000**	**HOMO→LUMO**	**0.69**
S_1	**1.91**	**648.7**	**15416**	**0.0374**	**HOMO→LUMO**	**0.69**
S_2	**2.44**	**507.6**	**19701**	**0.0048**	**HOMO→LUMO+1**	**0.70**

S_3	**3.03**	**409.3**	**24433**	**0.0530**	**HOMO-1→LUMO**	**0.68**
S_4	**3.15**	**393.2**	**25433**	**0.0352**	**HOMO-2→LUMO**	**0.68**
S_5	**3.39**	**366.1**	**27316**	**0.0094**	**HOMO→LUMO+2**	**0.69**
S_6	**3.44**	**360.0**	**27779**	**0.0505**	**HOMO→LUMO+3**	**0.69**
S_7	**3.54**	**350.7**	**28515**	**0.0176**	**HOMO→LUMO+4**	**0.67**
S_8	**3.59**	**345.7**	**28928**	**0.0026**	**HOMO-1→LUMO+1**	**0.59**
S_9	**3.59**	**345.1**	**28978**	**0.0117**	**HOMO-7→LUMO**	**0.45**
					HOMO-1→LUMO+1	**0.24**
					HOMO-6→LUMO	**0.23**
S_{10}	**3.64**	**340.3**	**29387**	**0.0158**	**HOMO→LUMO+5**	**0.45**
					HOMO-11→LUMO	**0.33**
					HOMO→LUMO+6	**0.21**

Table S7. Electronic transitions of dmp-pop calculated at the T_1 optimized geometry by TDDFT in Solvent DCM (CI > 0.20)

S_n/T_m	**Excitation energies (eV)**	**λ (nm)**	**Energy (cm^{-1})**	**f**	**Main configurations**	
T_1	**1.99**	**623.3**	**16044**	**0.0000**	**HOMO→LUMO**	**0.68**
S_1	**2.22**	**559.1**	**17886**	**0.0348**	**HOMO→LUMO**	**0.68**
S_2	**2.81**	**442.0**	**22625**	**0.0100**	**HOMO→LUMO+1**	**0.69**
S_3	**2.90**	**427.0**	**23420**	**0.0611**	**HOMO-1→LUMO**	**0.67**
S_4	**3.13**	**396.8**	**25202**	**0.0067**	**HOMO-2→LUMO**	**0.68**
S_5	**3.51**	**353.1**	**28321**	**0.0064**	**HOMO-1→LUMO+1**	**0.68**
S_6	**3.56**	**348.5**	**28695**	**0.0178**	**HOMO-4→LUMO**	**0.46**
					HOMO-5→LUMO	**-0.38**
S_7	**3.61**	**343.4**	**29121**	**0.0094**	**HOMO-5→LUMO**	**0.38**
					HOMO-6→LUMO	**-0.32**
					HOMO-4→LUMO	**0.29**
					HOMO-10→LUMO	**0.20**
S_8	**3.64**	**340.5**	**29369**	**0.0057**	**HOMO→LUMO+2**	**0.68**
S_9	**3.68**	**336.7**	**29701**	**0.0002**	**HOMO-3→LUMO**	**0.64**
S_{10}	**3.72**	**332.9**	**30040**	**0.0567**	**HOMO→LUMO+3**	**0.69**

Table S8. Electronic transitions of dbp-pop calculated at the T_1 optimized geometry by TDDFT in Solvent DCM (CI > 0.20)

S_n/T_m	Excitation energies (eV)	λ (nm)	Energy (cm^{-1})	f	Main configurations	
T_1	2.04	607.0	16475	0.0000	HOMO-1→LUMO	0.46
					HOMO→LUMO	0.40
					HOMO-2→LUMO	0.26
T_2	2.79	444.7	22488	0.0000	HOMO→LUMO+1	0.54
					HOMO-1→LUMO+1	0.35
S_1	3.03	408.6	24475	0.0285	HOMO→LUMO	0.67
S_2	3.22	385.2	25961	0.0037	HOMO-3→LUMO	0.58
					HOMO-1→LUMO	0.37
S_3	3.25	381.7	26199	0.0678	HOMO→LUMO+1	0.68
S_4	3.31	374.8	26682	0.0028	HOMO-2→LUMO	0.53
					HOMO-3→LUMO	0.27
					HOMO-1→LUMO	-0.23
					HOMO-3→LUMO+1	0.22
S_5	3.36	369.1	27094	0.0005	HOMO-3→LUMO+1	0.54
					HOMO-1→LUMO+1	0.34
					HOMO-2→LUMO	-0.23
S_6	3.49	355.4	28138	0.0105	HOMO-2→LUMO+1	0.62
					HOMO-1→LUMO+1	-0.21
					HOMO-3→LUMO+1	0.20
S_7	3.55	349.4	28621	0.2504	HOMO-1→LUMO	0.50
					HOMO-2→LUMO	0.34
					HOMO-3→LUMO	-0.27
S_8	3.64	340.9	29335	0.0014	HOMO-1→LUMO+1	0.53
					HOMO-3→LUMO+1	-0.31
					HOMO-2→LUMO+1	0.28
S_9	3.97	312.6	31991	0.0000	HOMO-4→LUMO	0.70
S_{10}	3.97	311.9	32063	0.0059	HOMO→LUMO+2	0.68

Table S9. SOC matrix elements $<T_m|H_{SOC}|S_n>(cm^{-1})$, the oscillator strengths f_n of $[Cu(phen)(POP)]^+$ calculated at the T_1^{opt} optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant (k_r/s^{-1}) is also given.

$E(T_1)=13398cm^{-1}$

	SOC	$E(S_n)$	$f(S_n)$	k_n
S_3	-56.8445	24433	0.0530	266.4958

S_4	-7.3201	25433	0.0352	2.3705
S_9	21.8027	28978	0.0117	3.6607
S_{10}	-55.9326	29387	0.0158	30.4613
k_r				302.9883

Table S10. SOC matrix elements $<T_m|H_{SOC}|S_n>$(cm^{-1}), the oscillator strengths f_n of $[Cu(dmp)(POP)]^+$ calculated at the T_1^{opt} optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant (k_r/s^{-1}) is also given.

E(T_1)=16044cm^{-1}

	SOC	E(S_n)	f(S_n)	k_n
S_3	15.9641	23420	0.0611	97.1573
S_4	-49.4996	25202	0.0067	61.7474
S_6	-5.1149	28695	0.0178	0.8062
S_7	-38.6065	29121	0.0094	22.3668
S_9	-16.2070	29701	0.0002	182.0776
k_r				364.1553

Table S11. SOC matrix elements $<T_m|H_{SOC}|S_n>$(cm^{-1}), the oscillator strengths f_n of $[Cu(dbp)(POP)]^+$ calculated at the T_1^{opt} optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant (k_r/s^{-1}) is also given.

E(T_1)=16475cm^{-1}

	SOC	E(S_n)	f(S_n)	k_n
S_1	-65.0599	24475	0.0285	662.9552
S_2	35.6793	25961	0.0037	17.3565
S_4	36.9834	26682	0.0028	11.8596
S_5	-12.1697	27094	0.0005	0.2293
S_7	14.2107	28621	0.2504	103.0932
k_r				795.4939

E(T_2)=22488cm^{-1}

	SOC	$E(S_n)$	$f(S_n)$	k_n
S_3	-28.9404	26199	0.0678	93.8309
S_4	18.8879	26682	0.0028	1.6207
S_5	63.0372	27094	0.0005	3.1745
S_6	51.1593	28138	0.0105	43.9091
S_8	19.3804	29335	0.0014	0.7760
k_r				143.3112

Table S12. Electronic transitions of dmp-pph3 calculated at the T_1 optimized geometry by TDDFT in Solvent DCM (CI > 0.20)

S_n/T_m	**Excitation energies (eV)**	**λ (nm)**	**Energy (cm^{-1})**	***f***	**Main configurations**	
T_1	**2.06**	**603.1**	**16582**	**0.0000**	**HOMO-1→LUMO**	**0.56**
					HOMO→LUMO	**-0.40**
T_2	**2.78**	**446.0**	**22422**	**0.0000**	**HOMO→LUMO+1**	**0.52**
					HOMO-1→LUMO+1	**-0.45**
S_1	**3.07**	**403.7**	**24772**	**0.0281**	**HOMO→LUMO**	**0.68**
S_2	**3.25**	**380.9**	**26254**	**0.0728**	**HOMO→LUMO+1**	**0.70**
S_3	**3.30**	**375.6**	**26625**	**0.0012**	**HOMO-3→LUMO**	**0.70**
S_4	**3.33**	**371.9**	**26890**	**0.0000**	**HOMO-2→LUMO**	**0.68**
S_5	**3.41**	**363.1**	**27541**	**0.0011**	**HOMO-3→LUMO+1**	**0.68**
S_6	**3.50**	**354.7**	**28194**	**0.0112**	**HOMO-2→LUMO+1**	**0.69**
S_7	**3.57**	**347.3**	**28794**	**0.2169**	**HOMO-1→LUMO**	**0.66**
S_8	**3.63**	**341.7**	**29266**	**0.0004**	**HOMO-1→LUMO+1**	**0.68**
S_9	**4.16**	**298.4**	**33513**	**0.0536**	**HOMO→LUMO+2**	**0.68**
S_{10}	**4.19**	**295.9**	**33796**	**0.0029**	**HOMO-8→LUMO**	**0.52**
					HOMO-12→LUMO	**0.25**
					HOMO-14→LUMO	**0.25**
					HOMO-13→LUMO	**0.20**

Table S13. SOC matrix elements $<T_m|H_{SOC}|S_n>$(cm^{-1}), the oscillator strengths f_n of $[Cu(dmp)(PPh_3)_2]^+$ calculated at the T_1^{opt} optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant (k_r/s^{-1}) is also given.

E(T_1)=16582cm^{-1}

	SOC	E(S_n)	f(S_n)	k_n
S_1	0.5513	24772	0.0281	0.0451
S_3	-22.9633	26625	0.0012	2.0682
S_7	0.4452	28794	0.2169	0.0879
S_{10}	27.2302	33796	0.0029	1.8846
k_r				4.0858

E(T_2)=22422cm^{-1}

	SOC	E(S_n)	f(S_n)	k_n
S_2	0.5513	26254	0.0728	1.2454
S_5	-22.9633	27541	0.0011	17.4411
S_6	0.4452	28194	0.0112	0.0513
S_8	27.2302	29266	0.0004	4.6950
k_r				23.4328