Thermally Activated Delayed Fluorescence (TADF) and Enhancing Photoluminescence Quantum Yields of $[Cu^{I}(diimine)(diphosphine)]^{+}$ Complexes – Photophysical, Structural, and Computational Studies

Charlotte L. Linfoot,[1] Markus J. Leitl,[2] Patricia Richardson,[1] Andreas F. Rausch,[2] Oleg Chepelin,[1] Fraser J. White,[1] Hartmut Yersin,*[2] and Neil Robertson*[1]

Supporting Information

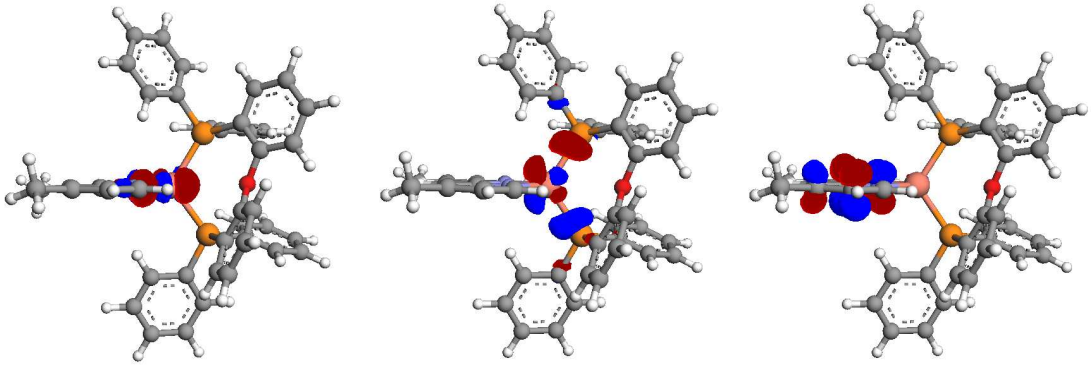

Fig. S1 Selected Molecular Orbitals for **1**

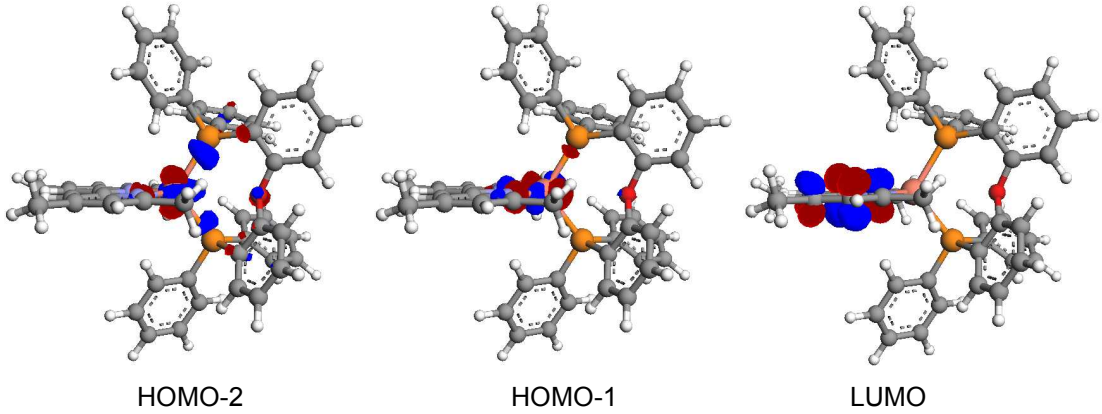

Fig. S2 Selected Molecular Orbitals for **2**

Table S1 Percentage contributions from component parts of **1** (in ethanol PCM) to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.

MO	Energy / eV	% Contribution from Cu-based MOs	% Contribution from POP-based MOs	% Contribution from bpy-based MOs
LUMO+12	-0.429	0.35	98.66	0.99
LUMO+11	-0.571	0.80	98.12	1.08
LUMO+10	-0.607	3.61	95.04	1.35
LUMO+9	-0.652	1.95	97.01	1.04
LUMO+8	-0.736	2.70	94.87	2.43
LUMO+7	-0.835	0.31	98.42	1.27
LUMO+6	-0.889	0.31	98.89	0.80
LUMO+5	-1.014	1.32	97.77	0.91
LUMO+4	-1.084	0.97	97.37	1.66
LUMO+3	-1.197	0.37	15.92	83.71
LUMO+2	-1.212	0.41	92.68	6.91
LUMO+1	-1.534	2.21	4.09	93.70
LUMO	-2.333	1.47	4.89	93.64
HOMO	-5.914	43.50	51.62	4.88
HOMO-1	-6.032	64.32	8.16	27.52
HOMO-2	-6.271	51.05	39.51	9.44
HOMO-3	-6.567	7.88	90.84	1.28
HOMO-4	-7.003	73.53	12.52	13.95
HOMO-5	-7.026	42.81	54.74	2.45
HOMO-6	-7.051	53.98	43.68	2.34
HOMO-7	-7.100	20.06	76.95	2.90
HOMO-8	-7.155	13.30	85.69	1.01
HOMO-9	-7.194	16.13	82.19	1.68
HOMO-10	-7.202	5.77	91.54	2.69
HOMO-11	-7.223	6.36	92.26	1.38
HOMO-12	-7.275	12.99	7.92	79.09

Table S2 TDDFT calculated visible absorption wavelengths for **1** (in ethanol PCM), indicating the molecular orbitals involved and their relative contribution to the absorption.

Absorbance / nm	Main Charge Transitions		Relative Contribution
	MO from	MO to	
419	HOMO	LUMO	100 %
394	HOMO-3	LUMO	14 %
	HOMO-2	LUMO	86 %
331	HOMO-6	LUMO	14 %
	HOMO-5	LUMO	11 %
	HOMO-4	LUMO	31 %
	HOMO	LUMO+1	44 %
330	HOMO-6	LUMO	18 %
	HOMO-5	LUMO	15 %
	HOMO-4	LUMO	33 %
	HOMO	LUMO+1	34 %
298	HOMO	LUMO+4	100 %
280	HOMO-12	LUMO	23 %
	HOMO-11	LUMO	9 %
	HOMO-9	LUMO	10 %
	HOMO-8	LUMO	15 %
	HOMO-4	LUMO+1	12 %
	HOMO-2	LUMO+2	13 %
	HOMO-2	LUMO+4	6 %
	HOMO-1	LUMO+5	12 %

Table S3 Percentage contributions from component parts of **2** (in ethanol PCM) to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.

MO	Energy / eV	% Contribution from Cu-based MOs	% Contribution from POP-based MOs	% Contribution from bpy-based MOs
LUMO+6	-0.949	0.37	98.43	1.20
LUMO+5	-1.017	1.02	67.72	31.26
LUMO+4	-1.039	1.17	91.07	7.76
LUMO+3	-1.085	0.60	57.63	41.77
LUMO+2	-1.244	0.40	95.85	3.75
LUMO+1	-1.371	1.21	4.46	94.33
LUMO	-2.261	1.44	4.17	94.39
HOMO	-5.863	50.89	36.87	12.24
HOMO-1	-6.100	61.15	19.32	19.53
HOMO-2	-6.328	51.88	38.93	9.19
HOMO-3	-6.502	12.61	85.39	2.00
HOMO-4	-6.913	53.86	7.58	38.56
HOMO-5	-6.960	85.99	10.54	3.47
HOMO-6	-7.019	33.39	26.58	40.03
HOMO-7	-7.070	7.75	77.74	14.51
HOMO-8	-7.137	15.94	82.27	1.79
HOMO-9	-7.152	20.09	76.13	3.78

Table S4 TD-DFT calculated visible absorption wavelengths for **2** (in ethanol PCM), indicating the molecular orbitals involved and their relative contribution to the absorption.

Absorbance / nm	Main Charge Transitions		Relative Contribution
	MO from	MO to	
447	HOMO-1	LUMO	41 %
	HOMO	LUMO	59 %
403	HOMO-1	LUMO	59 %
	HOMO	LUMO	41 %
380	HOMO-3	LUMO	20 %
	HOMO-2	LUMO	80 %
331	HOMO-5	LUMO	14 %
	HOMO-3	LUMO	18 %
	HOMO-1	LUMO+1	23 %
	HOMO	LUMO +1	45 %
310	HOMO-1	LUMO+1	52 %
	HOMO	LUMO+1	26 %
	HOMO	LUMO+2	12 %
	HOMO	LUMO+3	10 %
297	HOMO-7	LUMO	6 %
	HOMO-6	LUMO	16 %
	HOMO-4	LUMO	9 %
	HOMO-1	LUMO+2	19 %
	HOMO-1	LUMO+3	11 %
	HOMO-1	LUMO+5	6 %
	HOMO	LUMO+4	19 %
	HOMO	LUMO+5	14 %
288	HOMO-9	LUMO	10 %
	HOMO-6	LUMO	15 %
	HOMO-4	LUMO	7 %
	HOMO-2	LUMO +2	6 %
	HOMO-1	LUMO+3	22 %
	HOMO-1	LUMO+5	8 %
	HOMO	LUMO+3	7 %
	HOMO	LUMO+5	9 %
	HOMO	LUMO+6	16 %

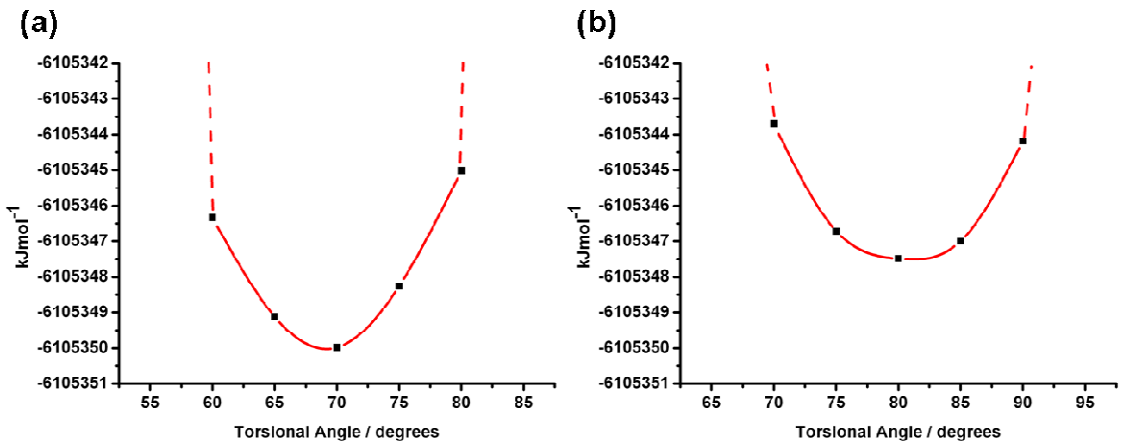

Figure S3 Plots of Torsional Angle against DFT calculated relative single-point triplet energies for (a) **2** starting from ArgusLab inputted structures and (b) **2** starting from crystal structure. Note that y-axes are the same range and scale and x-axes are the same scale, and that the curve is there to act as a guide to the eye.