Supplementary Information

Crystallographic Information

Table A. Crystallographic data for complexes **6**, **9** and **10**. Angles a - g defined in Figure A.

	6	**9**	**10**
bpy plane-H[†]	2.790	2.891	2.939
a	114.35(8)	114.11(8)	120.35(9)
b	120.27(17)	120.41(19)	119.49(19)
c	119.4(2)	120.5(2)	118.9(2)
d	114.82(17)	117.31(19)	116.42(19)
e	116.5(2)	116.4(2)	115.8(2)
f	118.90(17)	117.09(18)	118.15(19)
g	111.56(8)	109.38(8)	108.78(8)

[†]for **6** H=H18; for **9** H=H341; for **10** H=H271.

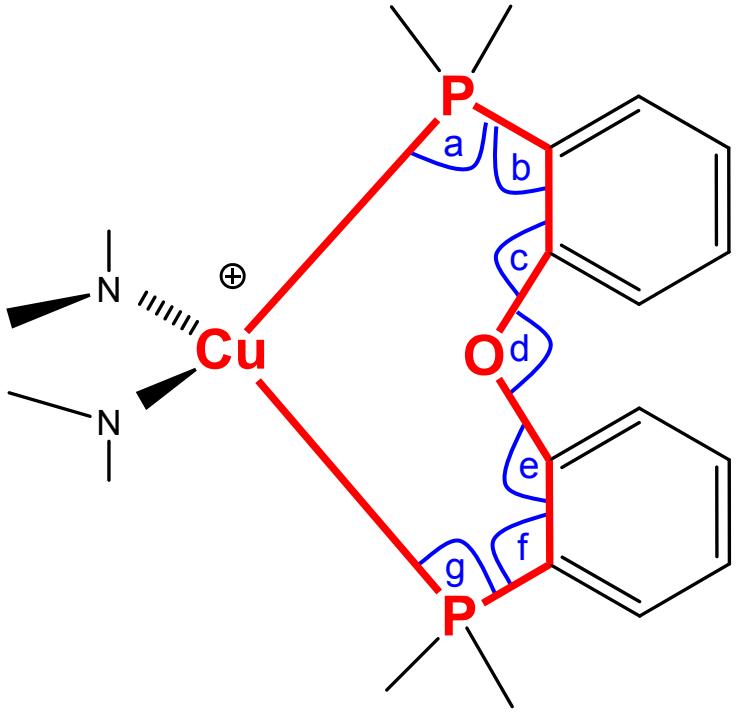

Figure A. Schematic of the POP chelate ring illustrating the angle labelling (a- g) for (Cu-P-C-C-O-C-C-P) in complexes **6**, **9** and **10**.

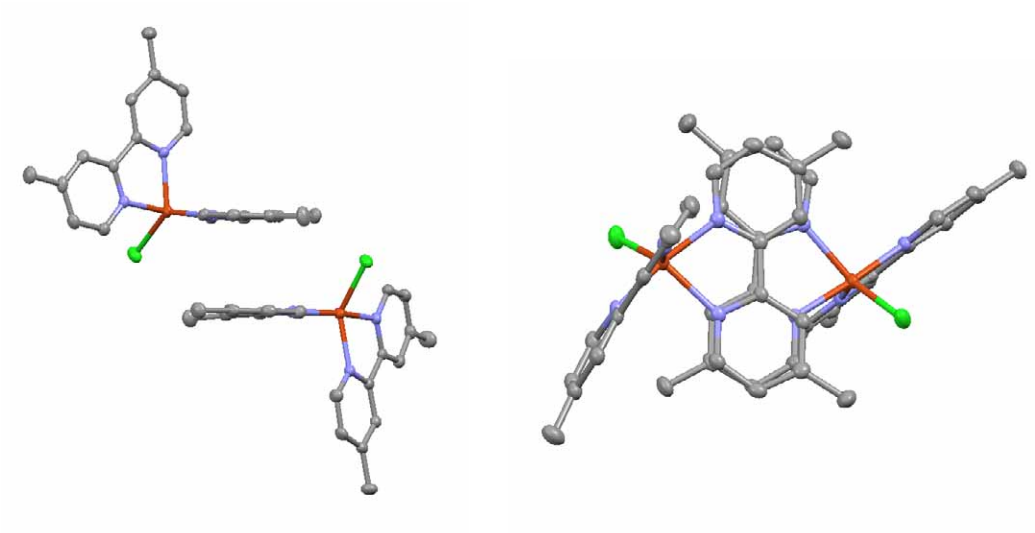

Figure B. Mercury plots of $[Cu(dmbpy)_2Cl][BF_4]$ demonstrating π–stacking interactions. Thermal ellipsoids are drawn at the 50% probability level. $[BF_4]$ counter ion omitted for clarity.

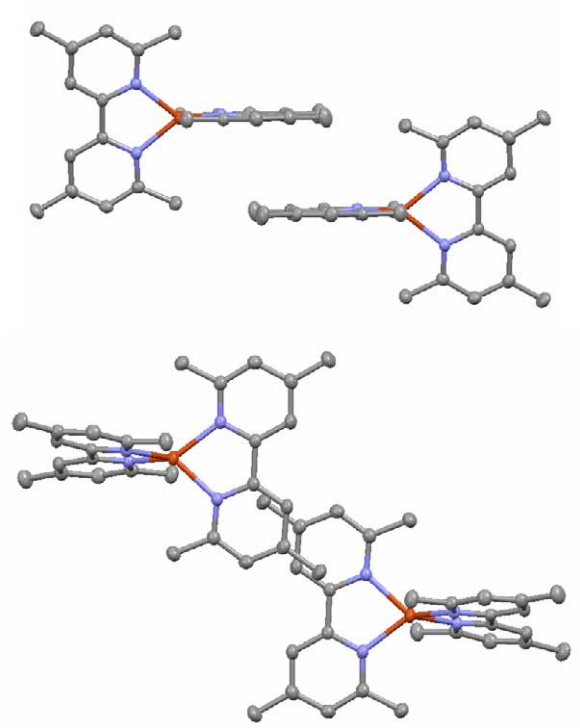

Figure C. Mercury plots of **1** demonstrating no π–stacking interactions. Thermal ellipsoids are drawn at the 50% probability level. $[BF_4]$ counter ion omitted for clarity.

Absorbance Spectroscopy

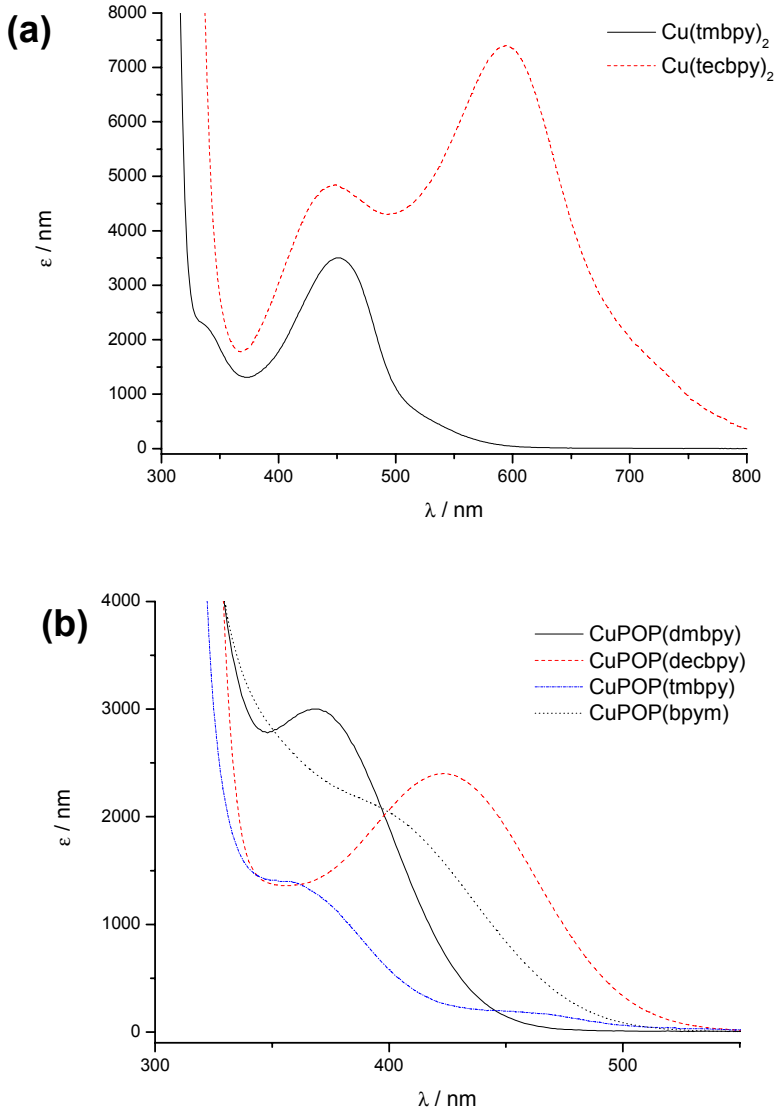

Figure D. (a) Absorbance Spectra for **1** and **3** (black line and red dashed line respectively). **1** carried out in DCM; **3** carried out in MeCN. (b) Absorbance Spectra for **4, 6, 7** and **9** (black line, red dashed line, blue dash/dotted line and black dotted line respectively). All carried out in MeCN.

Emission Spectroscopy

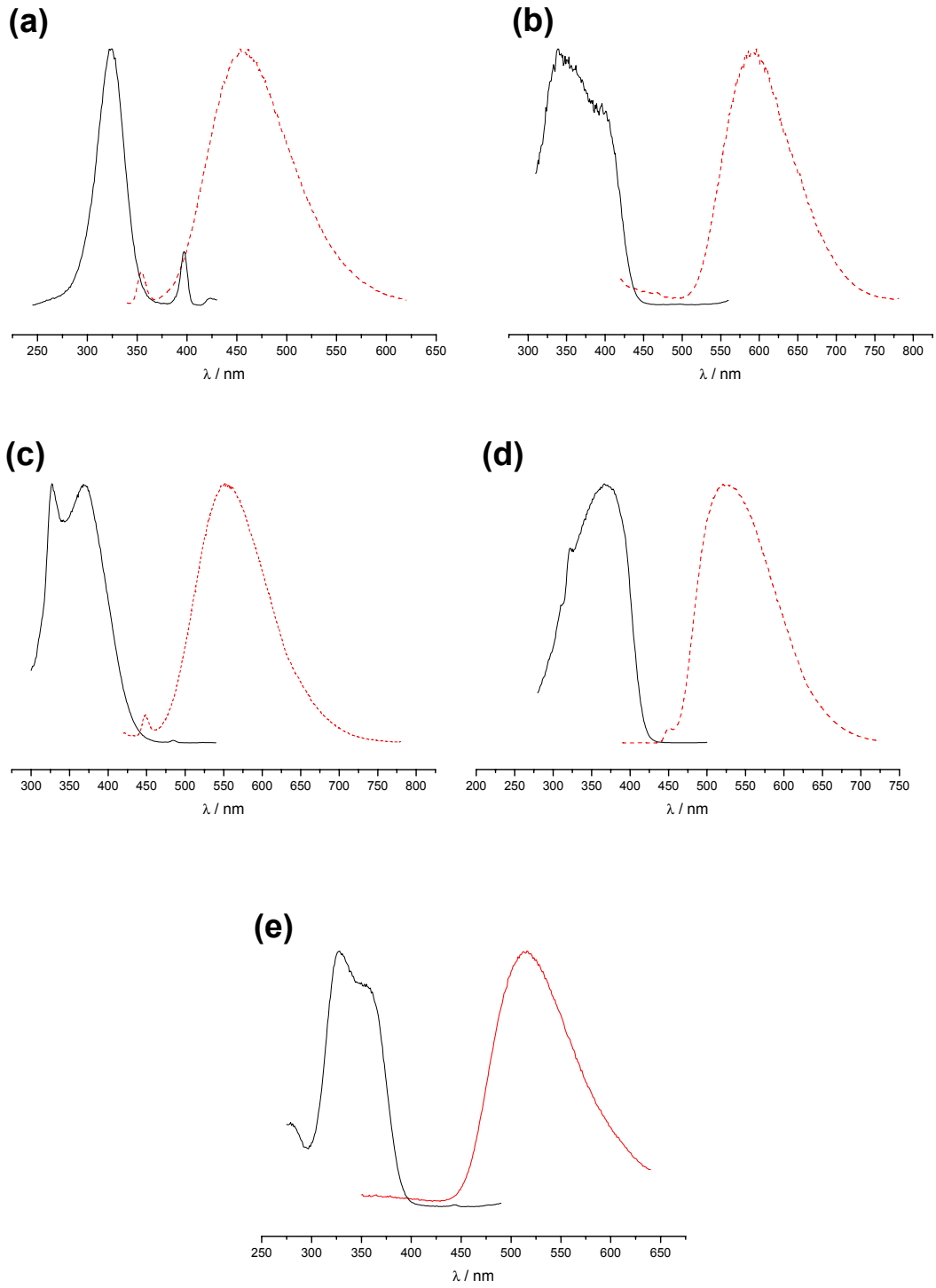

Figure E. Excitation and Emission Spectra for, (a) $[CuPOP(MeCN)_2][BF_4]$ at 300 K; (b) **4** at 77 K; (c) **7** at 300 K; (d) **7** at 77 K; (e) **9** at 77 K;. All in EtOH.

DFT and TD-DFT calculations

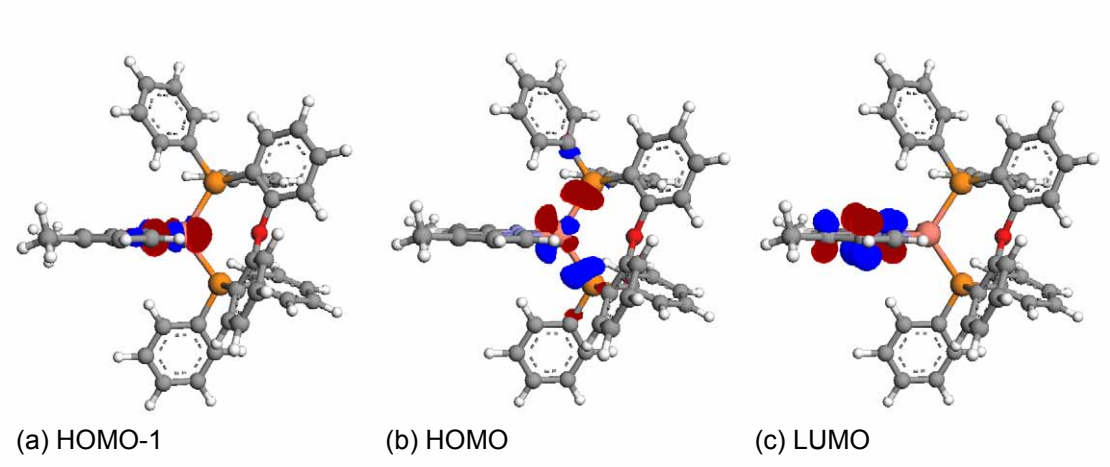

Figure F. Selected Molecular Orbital Images for **4;** (a) HOMO-1; (b) HOMO; (c) LUMO.

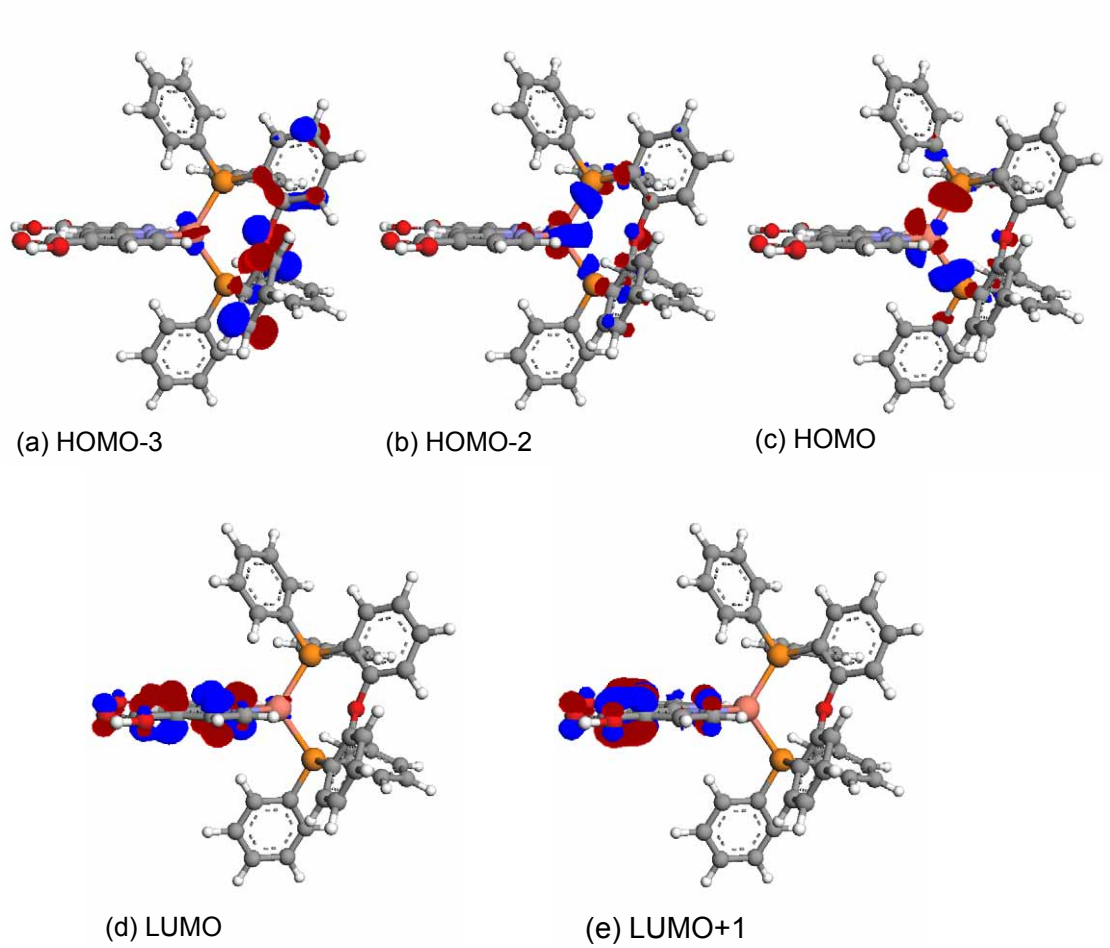

Figure G. Selected Molecular Orbital Images for **5;**
(a) HOMO-3; (b) HOMO-2; (c) HOMO; (d) LUMO; (e) LUMO+1.

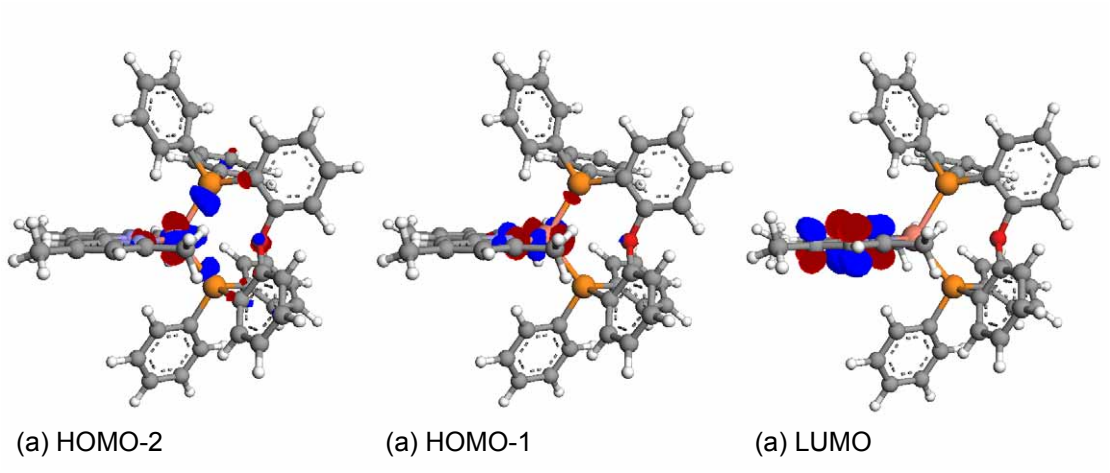

Figure H. Selected Molecular Orbital Images for **7;** (a) HOMO-2; (b) HOMO-1; (c) LUMO.

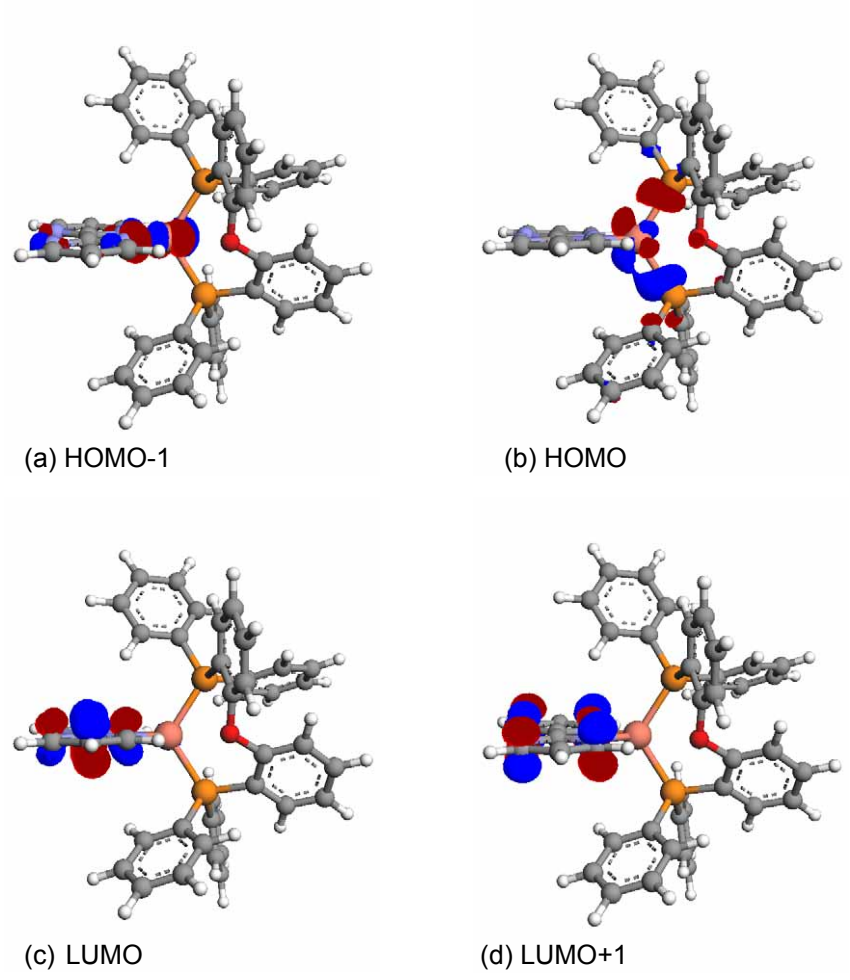

Figure I. Selected Molecular Orbital Images for **9;**
(a) HOMO-1; (b) HOMO; (c) LUMO; (d)LUMO+1.

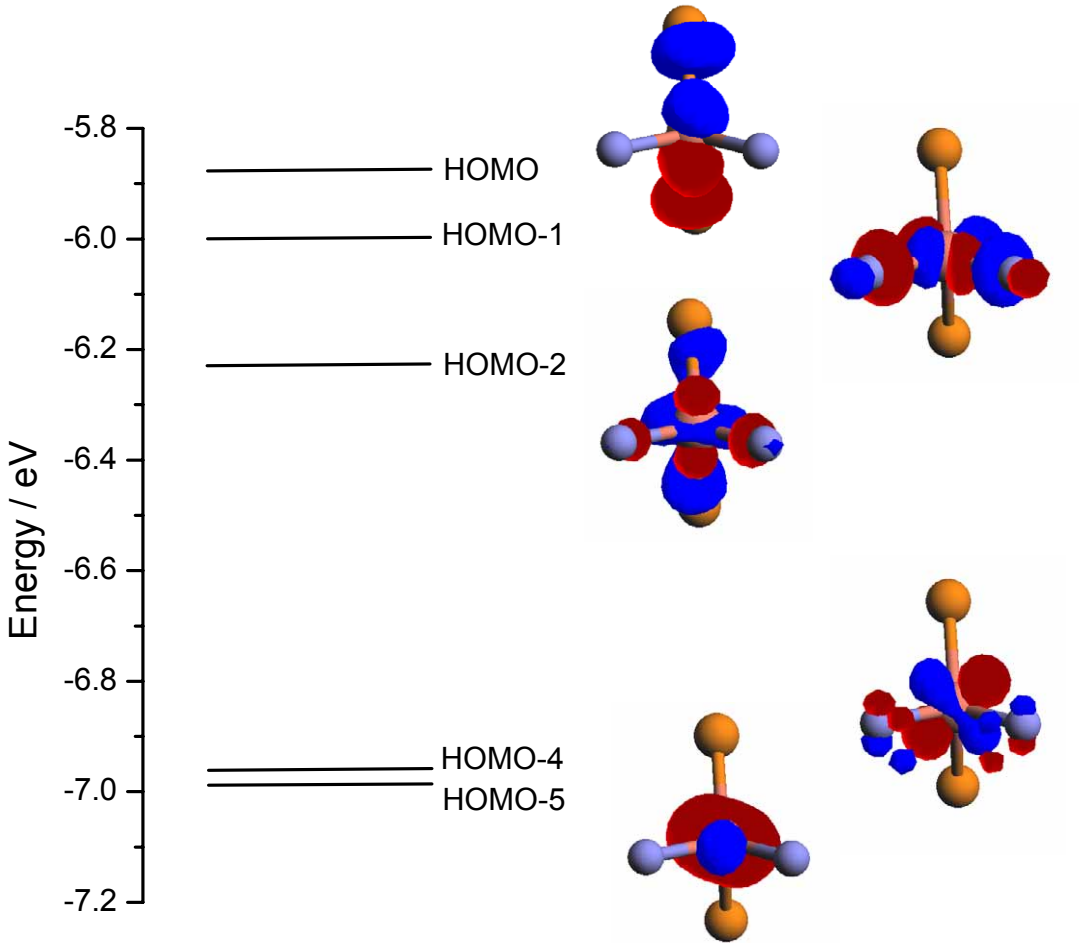

Figure J. Molecular Orbital Diagram for filled metal-based orbitals of **4.**

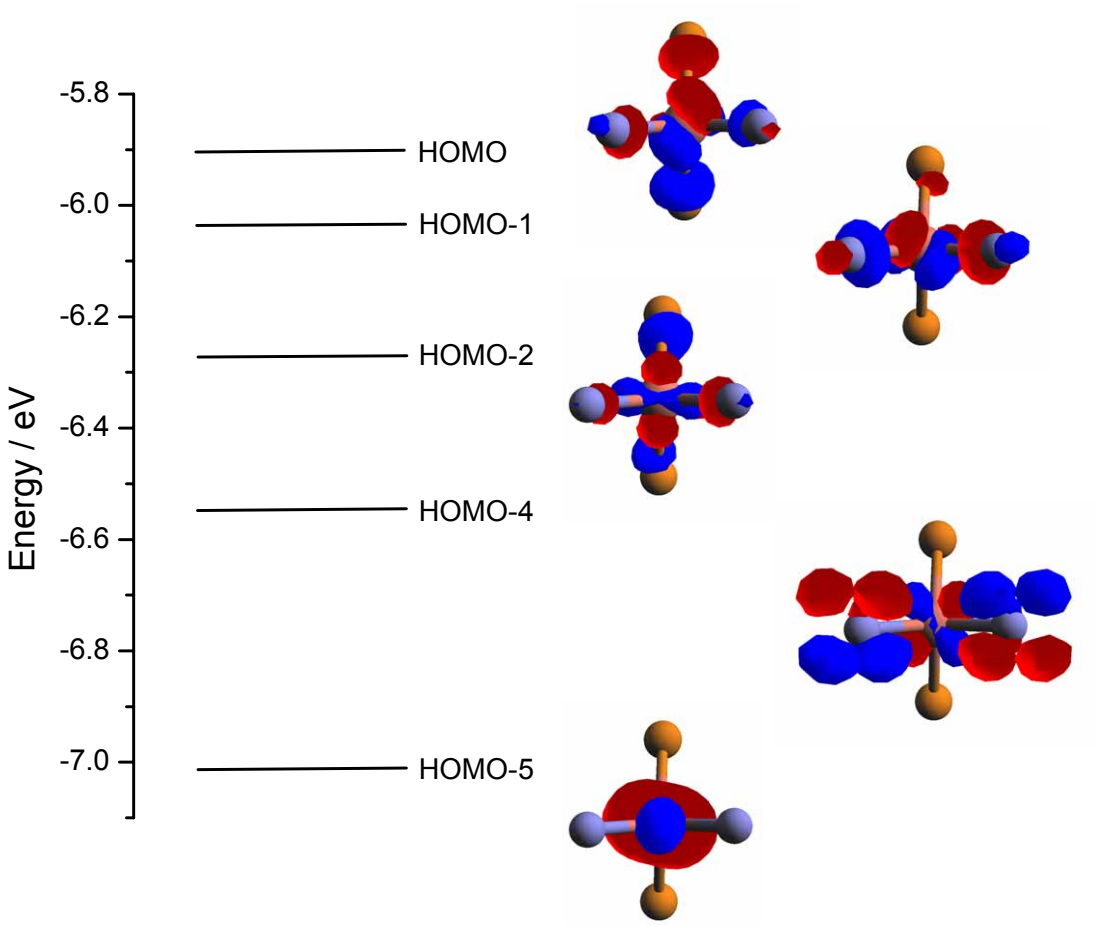

Figure K. Molecular Orbital Diagram for filled metal-based orbitals of **7**

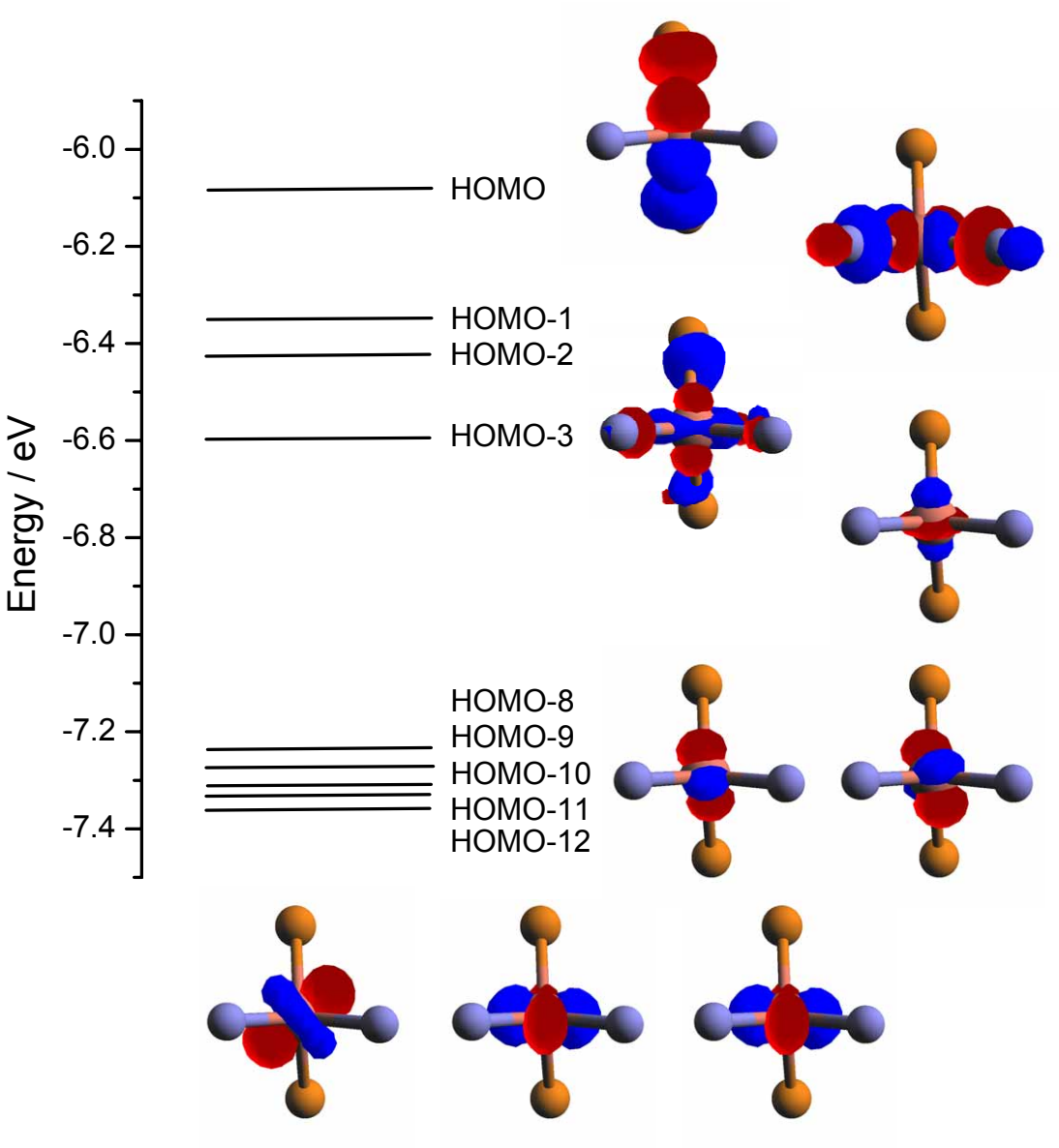

Figure L. Molecular Orbital Diagram for **5**

MO	Energy / eV	% Contribution from Cu-based MOs	% Contribution from POP-based MOs	% Contribution from bpy-based MOs
LUMO+10	-0.567	3.25	95.33	1.42
LUMO+9	-0.634	1.93	97.10	0.97
LUMO+8	-0.718	2.70	94.82	2.48
LUMO+7	-0.821	0.34	98.37	1.29
LUMO+6	-0.870	0.33	98.87	0.80
LUMO+5	-0.995	1.30	97.73	0.97
LUMO+4	-1.045	1.00	97.21	1.79
LUMO+3	-1.139	0.33	5.62	94.05
LUMO+2	-1.168	0.42	97.87	1.71
LUMO+1	-1.474	2.27	4.23	93.50
LUMO	-2.268	1.48	5.68	92.84
HOMO	-5.873	44.34	50.38	5.28
HOMO-1	-5.993	63.78	8.80	27.42
HOMO-2	-6.232	51.66	38.83	9.51
HOMO-3	-6.511	8.33	90.36	1.31
HOMO-4	-6.961	72.64	11.99	15.37
HOMO-5	-6.989	63.63	33.40	2.97
HOMO-6	-7.019	33.20	65.23	1.57
HOMO-7	-7.091	18.43	78.77	2.80
HOMO-8	-7.142	14.75	84.14	1.11
HOMO-9	-7.177	8.47	87.58	3.95
HOMO-10	-7.189	11.26	84.84	3.90
HOMO-11	-7.202	5.48	93.22	1.30
HOMO-12	-7.219	13.47	18.32	68.21

Table B. Percentage contributions from component parts of **4** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.

Absorbance / nm	Main Charge Transitions		Relative Contribution
	MO from	MO to	
416	HOMO-1	LUMO	16 %
	HOMO	LUMO	84 %
392	HOMO-3	LUMO	14 %
	HOMO-2	LUMO	86 %
340	HOMO-1	LUMO+1	82 %
	HOMO	LUMO+1	18 %
328	HOMO-6	LUMO	8 %
	HOMO-5	LUMO	14 %
	HOMO-4	LUMO	18 %
	HOMO-1	LUMO+1	11 %
	HOMO	LUMO+1	49 %
280	HOMO-12	LUMO	33 %
	HOMO-10	LUMO	10 %
	HOMO-9	LUMO	11 %
	HOMO-8	LUMO	11 %
	HOMO-4	LUMO+1	14 %
	HOMO-2	LUMO+2	13 %
	HOMO-2	LUMO+4	8 %

Table C. TD-DFT calculated visible absorption wavelengths for **4**, indicating the molecular orbitals involved and their relative contribution to the absorption.

MO	Energy / eV	% Contribution from Cu-based MOs	% Contribution from POP-based MOs	% Contribution from bpy-based MOs
LUMO+4	-1.108	0.98	96.59	2.43
LUMO+3	-1.232	0.50	98.35	1.15
LUMO+2	-2.223	0.40	1.13	98.47
LUMO+1	-2.604	0.40	0.53	99.07
LUMO	-3.158	2.57	4.25	93.18
HOMO	-6.083	36.98	58.41	4.61
HOMO-1	-6.347	65.77	7.37	26.86
HOMO-2	-6.424	38.48	54.01	7.51
HOMO-3	-6.595	14.09	83.47	2.44
HOMO-4	-7.042	1.26	98.47	0.27
HOMO-5	-7.176	11.88	87.18	0.94
HOMO-6	-7.198	7.77	91.73	0.50
HOMO-7	-7.226	1.81	97.67	0.52
HOMO-8	-7.269	20.74	77.43	1.83
HOMO-9	-7.234	28.29	69.38	2.33
HOMO-10	-7.309	69.95	22.78	7.27
HOMO-11	-7.331	54.99	42.99	2.02
HOMO-12	-7.359	39.89	57.20	2.91
HOMO-13	-7.383	5.67	93.85	0.48
HOMO-14	-7.487	4.45	94.40	1.15
HOMO-15	-7.537	16.79	81.94	1.27
HOMO-16	-7.622	4.05	90.70	5.25
HOMO-17	-7.653	6.61	6.22	87.17

Table D. Percentage contributions from component parts of **5** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.

Absorbance λ / nm	Main Charge Transitions		Relative Contribution
	MO from	MO to	
509	HOMO	LUMO	100 %
481	HOMO-3	LUMO	25 %
	HOMO-2	LUMO	75 %
440	HOMO-3	LUMO	29 %
	HOMO-2	LUMO	10 %
	HOMO	LUMO+1	61 %
383	HOMO-17	LUMO	64 %
	HOMO-16	LUMO	22 %
	HOMO-10	LUOM+2	14 %
281	HOMO	LUMO+4	100 %

Table E. TD-DFT calculated visible absorption wavelengths for **5**, indicating the molecular orbitals involved and their relative contribution to the absorption.

MO	Energy / eV	% Contribution from Cu-based MOs	% Contribution from POP-based MOs	% Contribution from bpy-based MOs
LUMO+6	-0.850	0.34	97.53	2.13
LUMO+5	-0.944	1.04	62.54	36.42
LUMO+4	-0.993	1.16	85.05	13.79
LUMO+3	-1.124	0.63	69.93	29.44
LUMO+2	-1.237	0.40	96.04	3.56
LUMO+1	-1.252	1.22	4.93	93.85
LUMO	-2.117	1.44	4.24	94.32
HOMO	-5.903	51.16	36.34	12.50
HOMO-1	-6.033	61.10	18.98	19.92
HOMO-2	-6.268	51.93	38.80	9.27
HOMO-3	-6.413	12.69	85.30	2.01
HOMO-4	-6.547	51.80	7.38	40.82
HOMO-5	-7.009	86.10	10.02	3.88
HOMO-6	-7.022	34.96	28.18	36.86

Table F. Percentage contributions from component parts of **7** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.

Absorbance λ / nm	Main Charge Transitions		Relative Contribution
	MO from	MO to	
446	HOMO-1	LUMO	42 %
	HOMO	LUMO	58 %
402	HOMO-1	LUMO	59 %
	HOMO-2	LUMO	41 %
378	HOMO-3	LUMO	21 %
	HOMO-2	LUMO	79 %
293	HOMO-6	LUMO	18 %
	HOMO-4	LUMO	11 %
	HOMO-2	LUMO+1	16 %
	HOMO-1	LUMO+2	37 %
	HOMO-1	LUOM+3	11 %
	HOMO-1	LUMO+5	7 %
288	HOMO-6	LUMO	13 %
	HOMO-1	LUMO+3	16 %
	HOMO-1	LUMO+5	8 %
	HOMO	LUMO+3	9 %
	HOMO	LUMO+4	11 %
	HOMO	LUMO+6	43 %

Table G. TD-DFT calculated visible absorption wavelengths for **7**, indicating the molecular orbitals involved and their relative contribution to the absorption.

MO	Energy / eV	% Contribution from Cu-based MOs	% Contribution from POP-based MOs	% Contribution from bpy-based MOs
LUMO+5	-1.037	0.36	99.05	0.59
LUMO+4	-1.173	0.33	98.93	0.74
LUMO+3	-1.238	0.75	98.18	1.07
LUMO+2	-2.015	0.35	1.81	97.84
LUMO+1	-2.273	1.97	3.41	94.62
LUMO	-2.921	1.47	3.80	94.73
HOMO	-6.067	38.12	56.37	5.51
HOMO-1	-6.333	59.87	12.00	28.13
HOMO-2	-6.498	48.57	42.12	9.31
HOMO-3	-6.784	4.63	94.22	1.15
HOMO-4	-7.166	8.35	90.47	1.18
HOMO-5	-7.187	3.07	96.66	0.27
HOMO-6	-7.227	5.71	93.94	0.35

Table H. Percentage contributions from component parts of **9** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.

Absorbance λ / nm	Main Charge Transitions		Relative Contribution
	MO from	MO to	
516	HOMO-1	LUMO	63 %
	HOMO	LUMO	37 %
481	HOMO-1	LUMO	37 %
	HOMO	LUMO	63 %
447	HOMO-2	LUMO	100 %
400	HOMO-1	LUMO+1	54 %
	HOMO	LUMO+1	46%
383	HOMO-1	LUMO+1	46 %
	HOMO	LUMO+1	54 %
291	HOMO	LUMO+4	100 %
281	HOMO-6	LUMO+1	13 %
	HOMO-1	LUMO+3	69 %
	HOMO	LUMO+5	18 %

Table I. TD-DFT calculated visible absorption wavelengths for **9**, indicating the molecular orbitals involved and their relative contribution to the absorption.

Solar Cell Measurements: I-V Characterisation

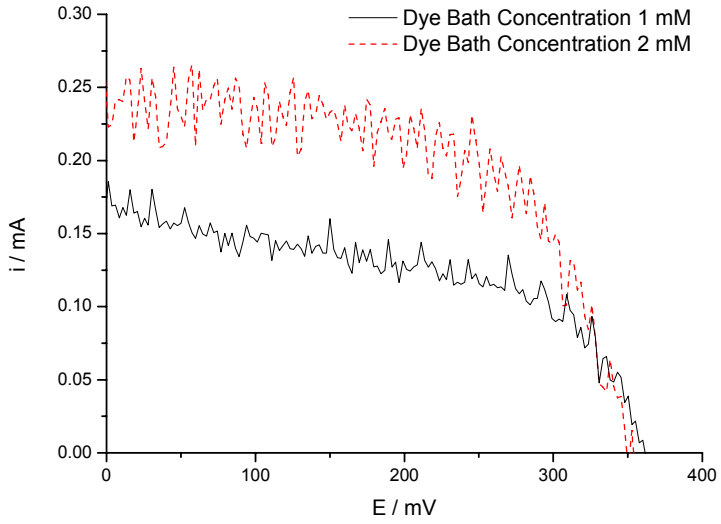

Figure M. *I-V* Curve for **5.** Black solid line = Dye Bath concentration 1 mM; red dashed line = dye bath concentration 2 mM.

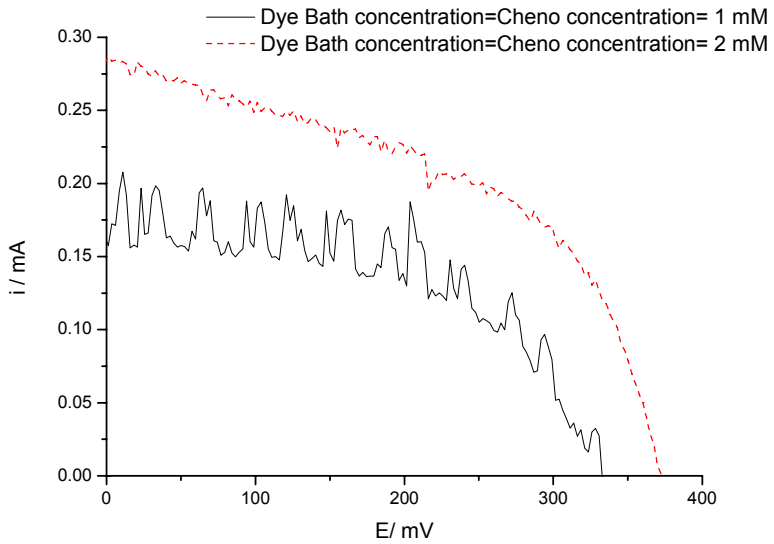

Figure N. *I-V* Curve for **5**. Black solid line = Dye Bath and Cheno concentration is 1 mM; red dashed line = Dye Bath and Cheno concentration is 2 mM.

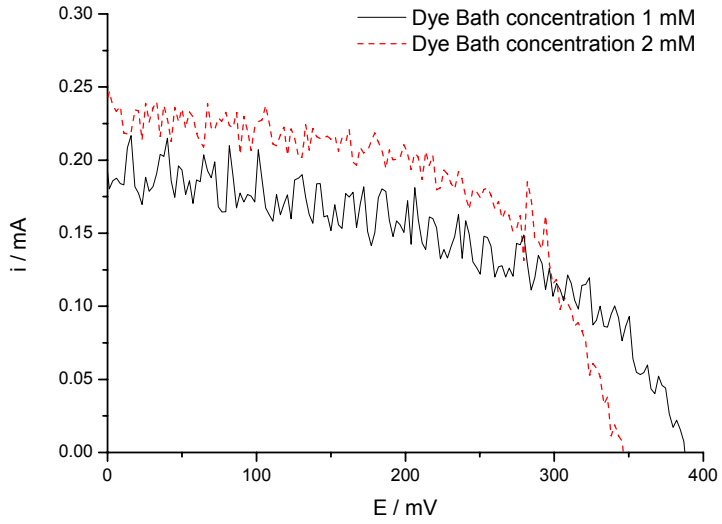

Figure O. *I-V* Curve for **5**. Black solid line = $TiCl_4$ post-treatment used with Dye Bath concentration of 1 mM; red dashed line = $TiCl_4$ post-treatment used with Dye Bath concentration 2 mM.