Electronic Supplementary Material (ESI) for Dalton Transactions

Polymorph and isomer conversion of complexes based on CuI and PPh_3 easily observed *via* luminescence

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Supplementary Information

7 pages

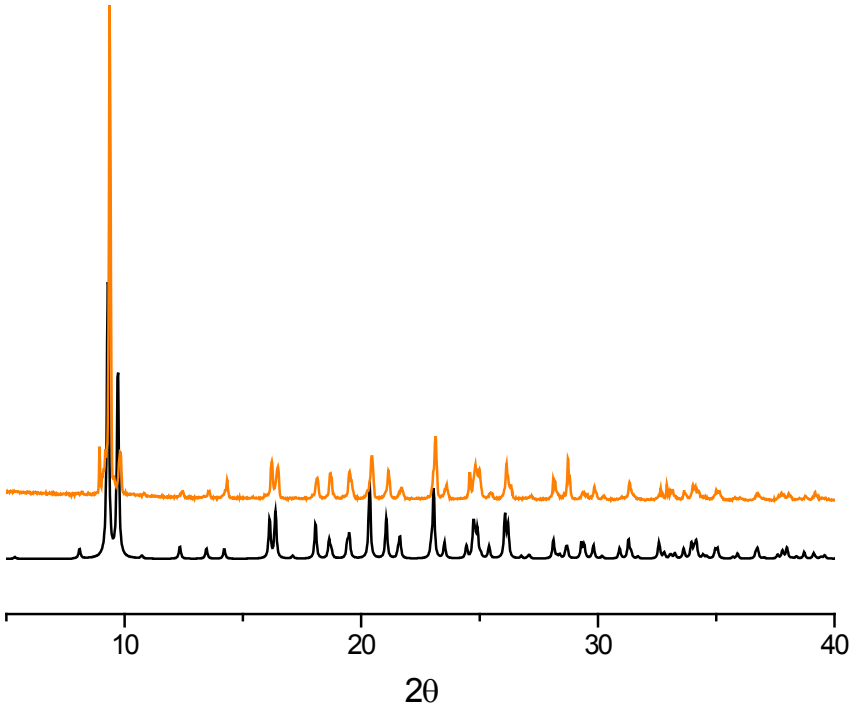

Figure S1: experimental and calculated diffraction pattern comparison for $[CuI(PPh_3)_3]\alpha$

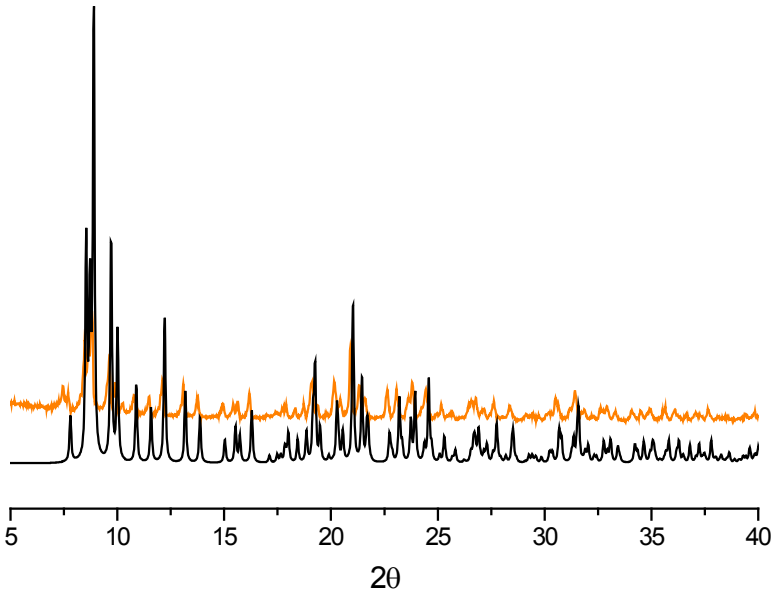

Figure S2: experimental and calculated diffraction pattern comparison for $[Cu_2I_2(PPh_3)_3]$

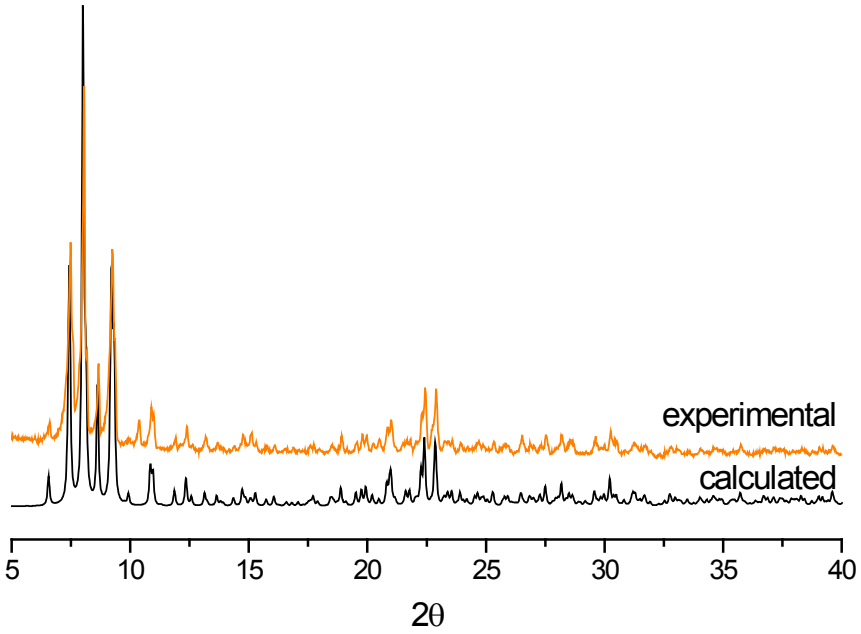

Figure S3: experimental and calculated patter comparison for $[CuI(PPh_3)]_4$**1a**

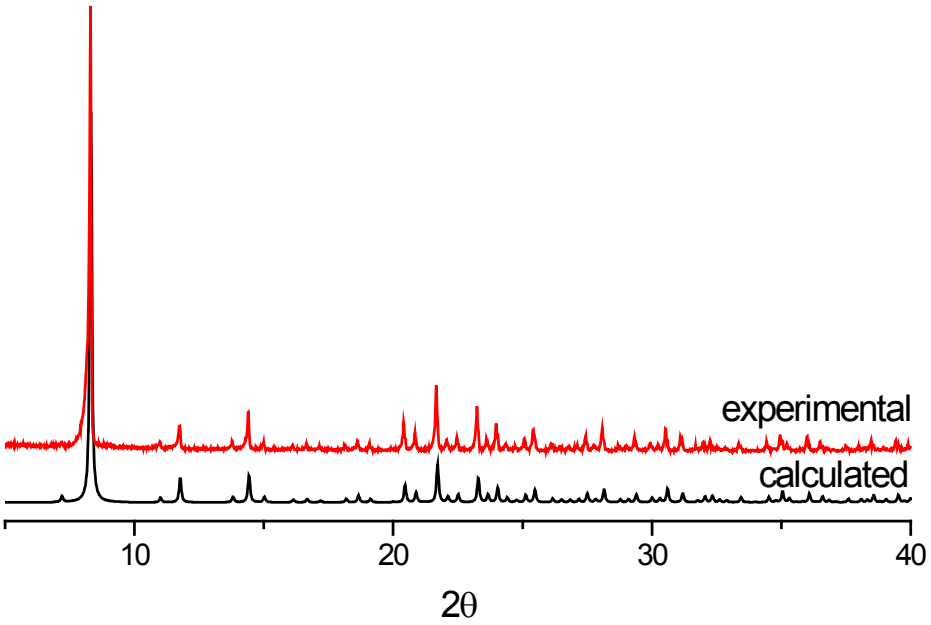

Figure S4: experimental and calculated patter comparison for $[CuI(PPh_3)]_4$**1b**

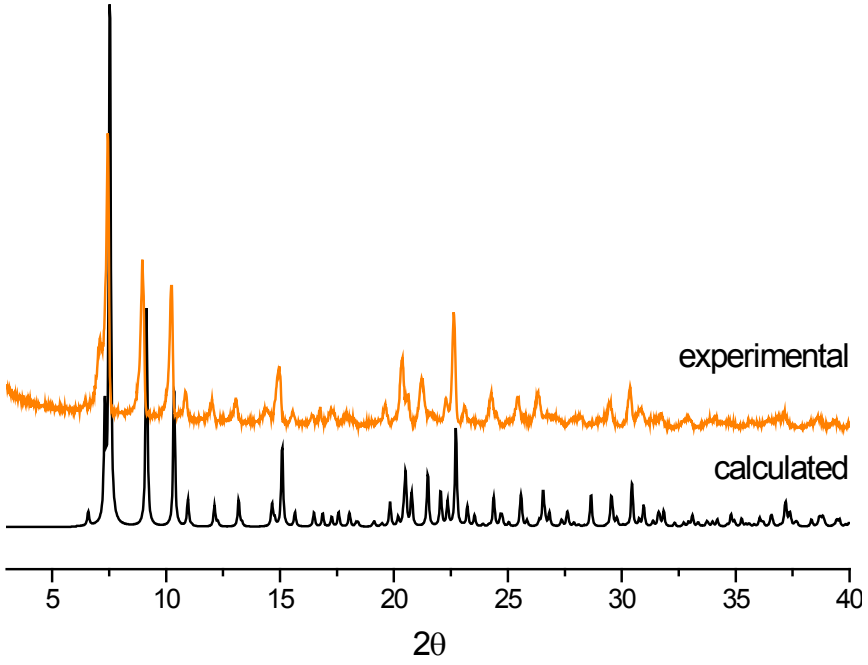

Figure S5*:* experimental and calculated patter comparison for $[CuI(PPh_3)]_4$**2**

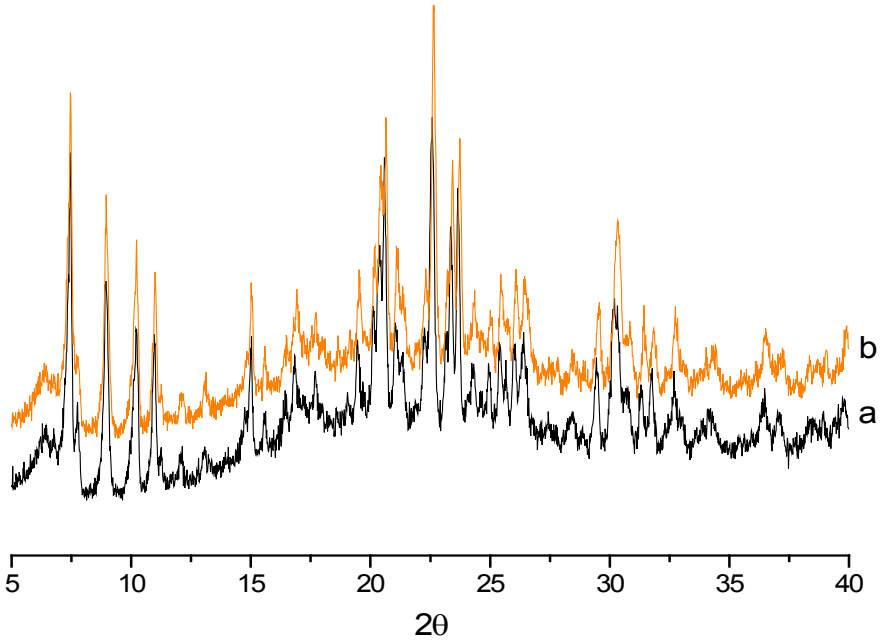

Figure S6*:* experimental and calculated patter comparison for $[CuI(PPh_3)]_4$**2**

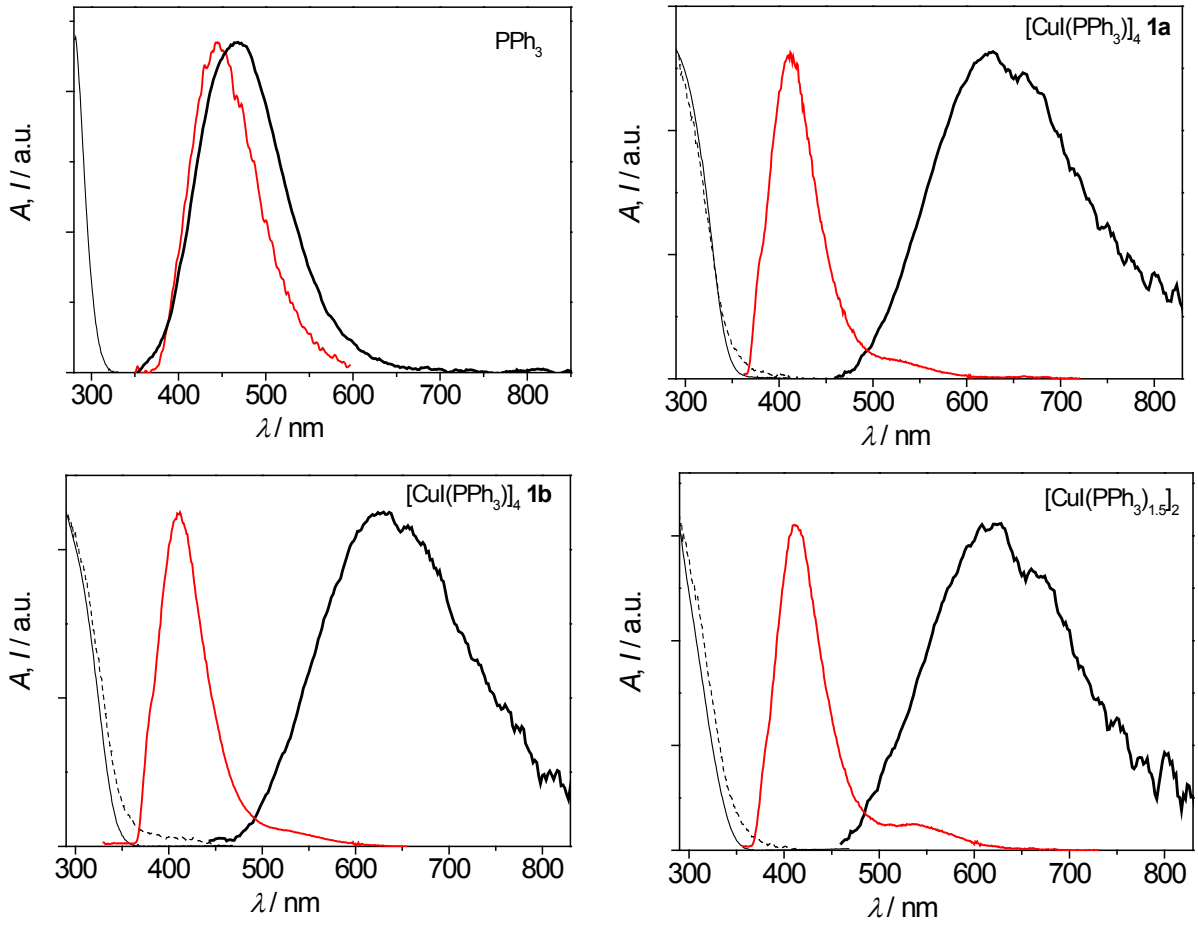

Figure S7: arbitrarily scaled absorption (black thin) and room temperature (black thick) and 77K (red) corrected emission spectra of toluene solutions of PPh_3 and compounds $[Cu_4I_4(PPh_3)_4]$ **1a**, $[Cu_4I_4(PPh_3)_4]$ **1b** and $[CuI(PPh_3)_{1.5}]_2$; excitation at 300 nm for PPh_3 and 330 nm for the Cu(I) complexes. The room temperature excitation spectra of the complexes measured at 620 nm are also reported (dash).

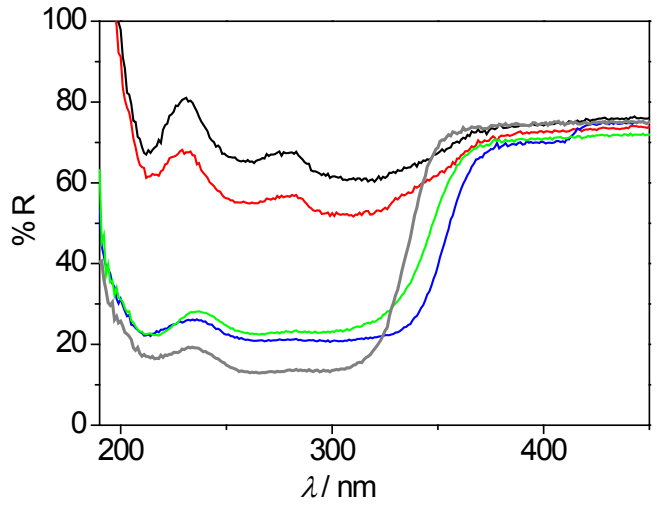

Figure S8: reflectance spectra of solid samples of PPh_3 (grey), $[Cu_4I_4(PPh_3)_4]$**1b** (black), $[Cu_4I_4(PPh_3)_4]$**1a** (red), $[CuI(PPh_3)]_4$ **2** (blue) and $[CuI(PPh_3)_{1.5}]_2$ (green).

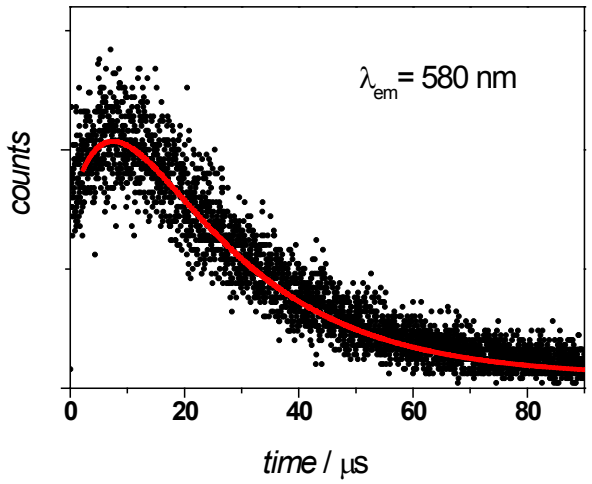

Figure S9: luminescence profile at 580 nm of solid $[Cu_4I_4(PPh_3)_4]$ **1a** at 77 K and the bi-exponential fitting (red).

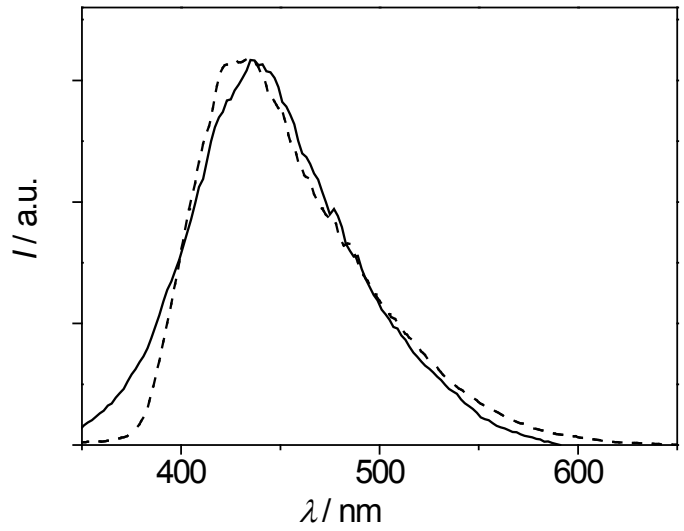

Figure S10: normalized corrected emission spectra of solid PPh_3 at room temperature (solid line) and 77 K (dashed line). Excitation at 300 nm.

Table S1. Crystal data and details of measurement for compound crystallized in this work.

	$[CuI(PPh_3)_3]$**1b**	$[Cu_4I_4(PPh_3)_4]$**1a**	$[Cu_4I_4(PPh_3)_4]$**1b**	$[CuI(PPh_3)_2]_{1.5}*CH_2Cl_2$
Chemical formula	$C_{54}H_{45}CuIP_3$	$C_{72}H_{60}Cu_4I_4P_4$	$C_{72}H_{60}Cu_4I_4P_4$	$C_{55}H_{47}Cl_2Cu_2I_2P_3$
M_r	977.25	1811.85	1810.84	1252.62
Crystal system	Monoclinic	Monoclinic	Cubic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	I-43d	$P2_1/c$
T [K]	RT	90	90	RT
a [Å]	13.2375 (5),	13.4237 (10)	29.7864 (3)	15.7252(6)
b [Å]	18.5976 (7)	26.406 (3)		19.5305(7)
c [Å]	18.9297 (7)	19.4266 (11)		17.6410(8)
β (°)	93.953 (4)	99.531 (7)		110.473(5)
V (Å^3)	4649.1 (3)	6791.0 (9)	26427.4 (5)	5075.7(4)
Z	4	4	16	4
F (000)	1984	3524	14080	2480
ϑ range [°]	2.68 – 29.02	2.78 – 29.18	2.56 – 29.01	2.68 – 29.09
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	1.27	3.19	3.28	2.29
Measured reflns	24269	35458	13317	32388
Unique reflns	10549	15590	4275	11167
Parameters	424	758	253	578
GOF on F^2	0.76	1.04	1.02	1.23
R_{int}	0.035	0.100	0.046	0.072
R_1(on F, [I> 2σ(I)])	0.044	0.046	0.038	0.106
$wR(F^2)$	0.130	0.112	0.061	0.323