Electronic Supplementary Information

A new class of luminescent Cu(I) complexes with tripodal ligands – TADF emitters for the yellow to red color range

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Discussion of the crystal structure of tpyas

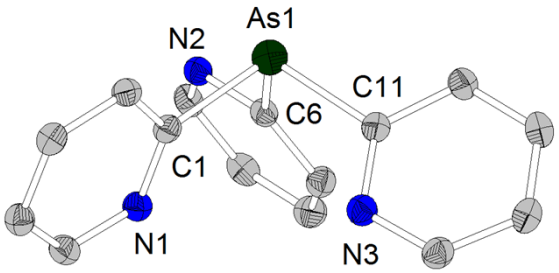

Figure S1 Molecular structure for **tpyas** (thermal ellipsoids with 50 % probability). Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: **As1-C1** 1.964(2), **As1-C6** 1.963(2), **As1-C11** 1.971(2), **As1-C1-N1** 119.8(2), **As1-C6-N2** 111.0(2), **As1-C11-N3** 120.1(2), **C1-As1-C6** 97.5(1), **C1-As1-C11** 99.2(1), **C6-As1-C11** 100.0(1).

Single crystals of tpyas have been obtained by slow evaporation of a saturated solution in acetone. The molecule shows a pyramidal molecular geometry with As-C bond distances from 1.963(2) Å to 1.971(2) Å which are only minimally longer than such for triphenylarsine (1.942(11) Å to 1.956(11) Å).[1] Also the bond angles C-As-C varying from 97.5 (1)° to 100.0(1)° are in good agreement with the corresponding angles of triphenylarsine. The three pyridine rings of tpyas are oriented in a way that the nitrogen atoms of two rings point away from the lone pair of the arsenic atom and the nitrogen atom of one ring points in the direction of the lone pair of the arsenic atom. This structural feature is already literature-known from tpyp.[2] The three As-C-N-angles differ significantly. The angle As1-C6-N2 111.0 (2)° is much smaller than the other two angles As1-C1-N1 and As1-C11-N3 with 119.8(2)° or 120.1(2)°. This phenomenon was also observed in the molecular structure of tpyp.[2]

[1] M.-U.-Haque, H. A. Tayim, J. Ahmed, W. Horne, *J. Cryst. Spectrosc.*, 1985, **15**, 561-571.
[2] R. Keene, M. R. Snow, E. R. T. Tiekink, *Acta Cryst.*, 1988, **C44**, 757-758.

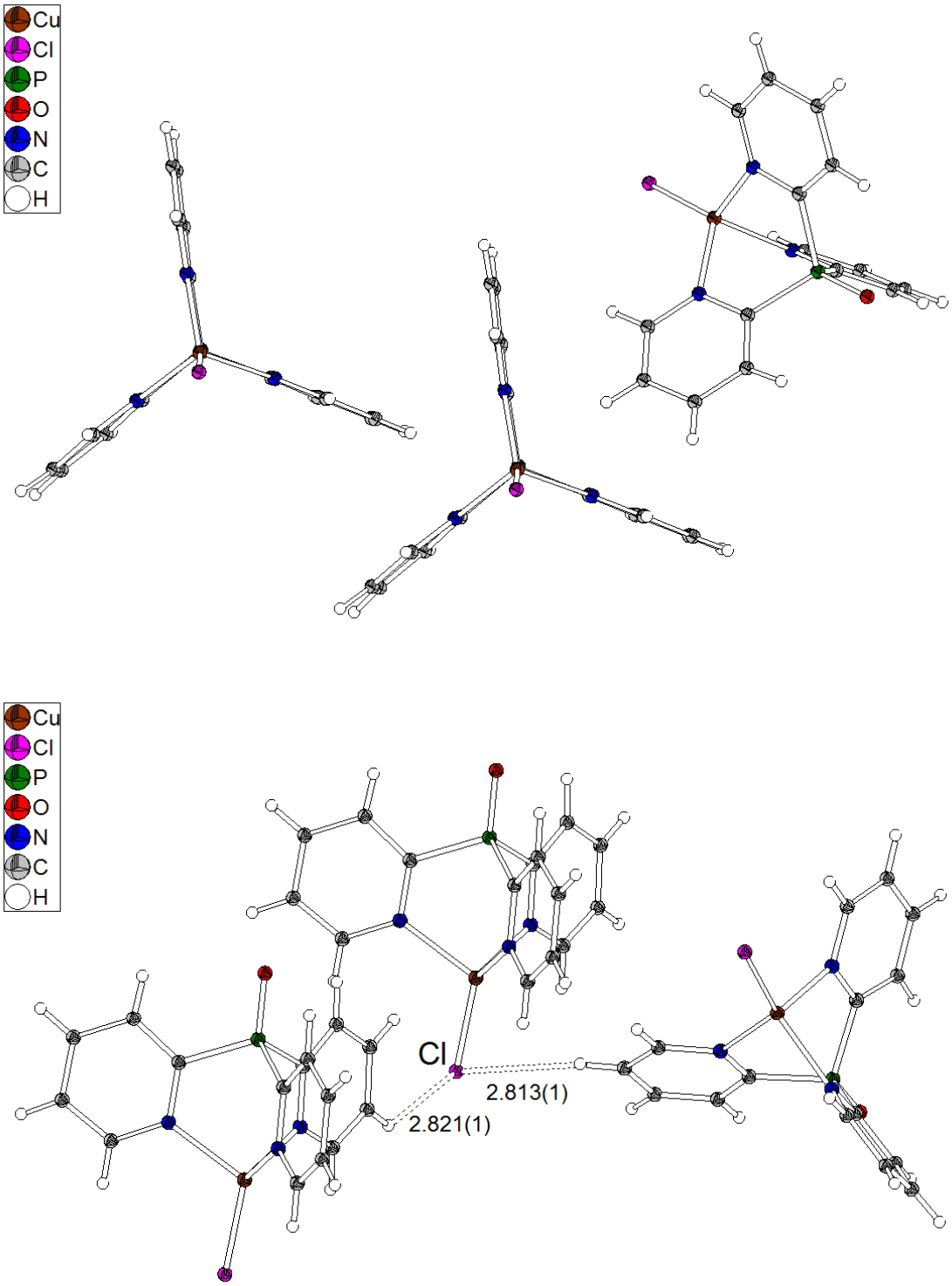

Figure S2 Part of the crystal structure of [CuCltpypo] **C1** (thermal ellipsoids with 50 % probability) from different perspectives (above and below). Solvent molecules are omitted for clarity. Distances between the chloride and nearest hydrogen atoms of neighboring molecules in [Å].

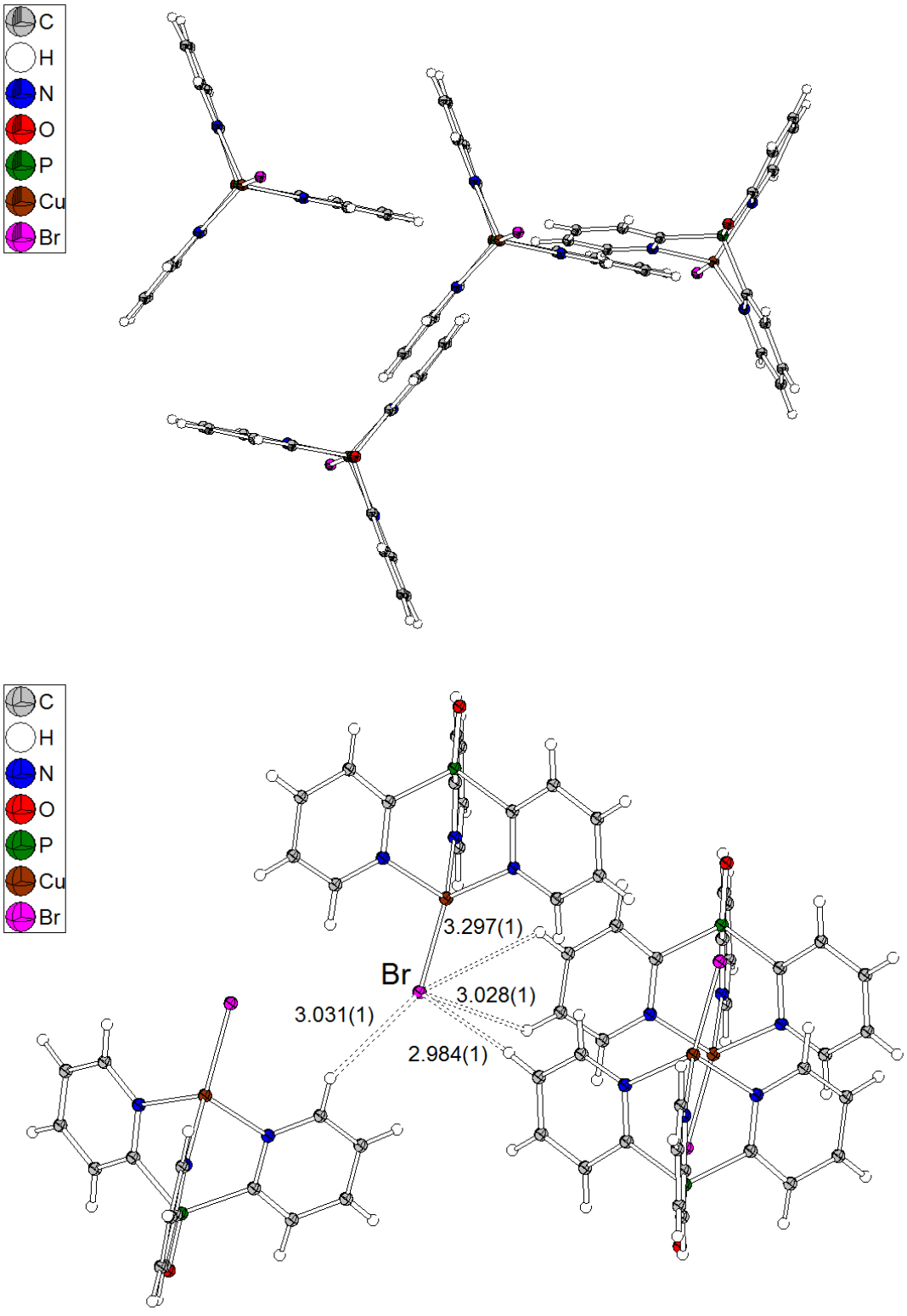

Figure S3 Part of the crystal structure of [CuBrtpypo] **C2** (thermal ellipsoids with 50 % probability) from different perspectives (above and below). Solvent molecules are omitted for clarity. Distances between the bromide and nearest hydrogen atoms of neighboring molecules in [Å].

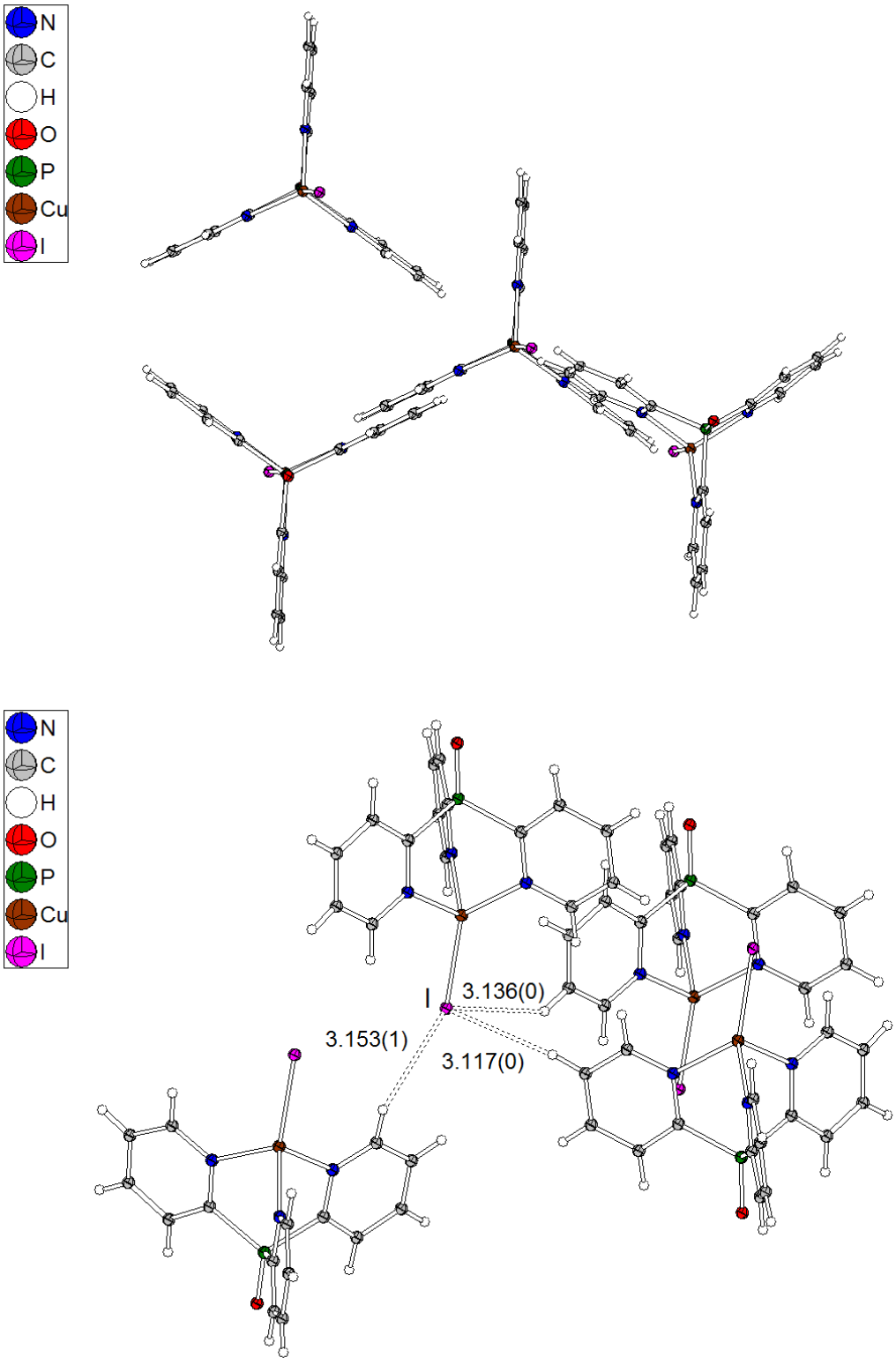

Figure S4 Part of the crystal structure of [CuItpypo] **C3** (thermal ellipsoids with 50 % probability) from different perspectives (above and below). Solvent molecules are omitted for clarity. Distances between the iodide and nearest hydrogen atoms of neighboring molecules in [Å].

Table S1 Selected calculated bond distances [Å] and angles [°] for the ground state (S_0) and the first triplet state (T_1) geometry of [CuItpypo] **C3**, [CuItpyaso] **C8** and [CuItpym] **C9**.

	S_0 (C3)	T_1 (C3)	S_0 (C8)	T_1 (C8)	S_0 (C9)	T_1 (C9)
Cu1-N1	2.146	2.265	2.157	2.291	2.163	2.262
Cu1-N2	2.145	1.986	2.157	1.991	2.162	1.975
Cu1-N3	2.144	1.985	2.158	1.989	2.159	1.974
Cu1-I1	2.521	2.493	2.528	2.497	2.502	2.487
I1-Cu1-N1	122.7	110.3	121.1	108.6	127.4	112.6
I1-Cu1-N2	122.9	127.4	121.1	126.1	127.2	130.5
I1-Cu1-N3	123.1	128.3	121.3	127.0	127.4	131.4
N1-Cu1-N2	93.2	94.3	95.7	96.5	87.0	89.7
N1-Cu1-N3	93.4	94.2	95.6	96.4	87.1	89.6
N2-Cu1-N3	93.2	93.3	95.7	95.0	87.1	90.0

Table S2 Calculated molecular orbital energies (in eV) for the ground state geometry

	HOMO	LUMO	Gap
[CuCltpypo] **C1**	−4.80	−2.18	2.62
[CuBrtpypo] **C2**	−4.85	−2.21	2.64
[CuItpypo] **C3**	−4.79	−2.25	2.54
[CuItpyps] **C6**	−4.83	−2.31	2.52
[CuItpypse] **C7**	−4.85	−2.34	2.51
[CuItpyaso] **C8**	−4.87	−2.18	2.69
[CuItpym] **C9**	−4.47	−1.78	2.69

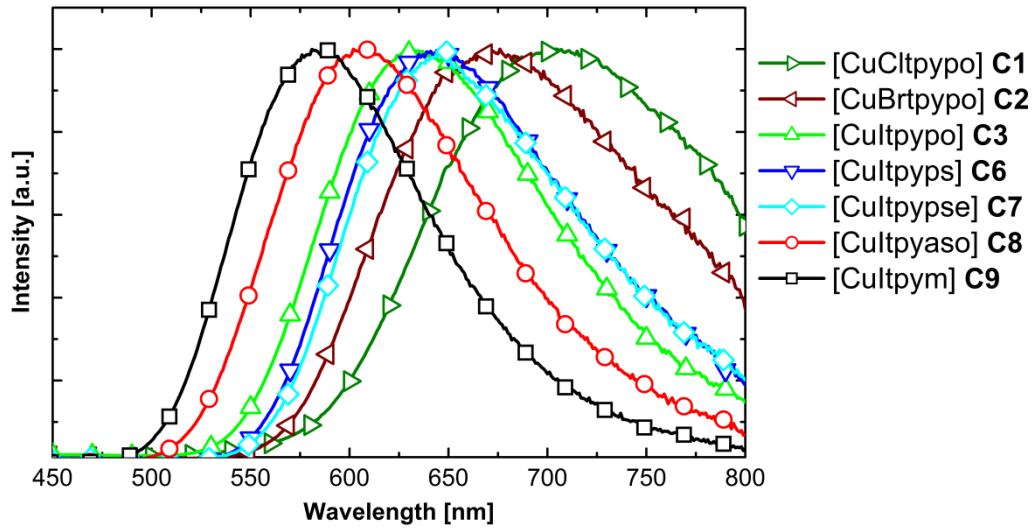

Figure S5 Emission spectra of compounds C1 – C3 and C6 – C9 doped into a PMMA matrix. All spectra recorded at ambient conditions. Excitation at λ_{exc} = 350 nm.

Table S3 Calculated transition energies for the optimized triplet geometry. In addition, the experimentally (exp.) found emission energies for the complexes doped into a PMMA matrix at ambient temperature are displayed.

	Transition energy [nm] ($S_1 \rightarrow S_0$)	Transition energy [nm] ($T_1 \rightarrow S_0$)	$\Delta E(S_1\text{-}T_1)$ [cm^{-1}]	Transition energy [nm] (exp.)
[CuCltpypo] **C1**	1075	1254	1328	710
[CuBrtpypo] **C2**	977	1119	1299	675
[CuItpypo] **C3**	924	1026	1076	635
[CuItpyps] **C6**	935	1040	1080	650
[CuItpypse] **C7**	943	1049	1072	650
[CuItpyaso] **C8**	835	916	1059	610
[CuItpym] **C9**	833	924	1182	585