Electronic Supplementary Information (ESI) for

Interconversion between ladder-type octanuclear and linear tetranuclear copper(I) complexes supported by tetraphosphine ligands

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Fig. S1. ORTEP for complex \([\text{Cu}_8(\mu-I)_2(\mu_3-I)_6(\mu-dppm)_2]\) (1c).

Fig. S2. \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of 1a, 1b and 2 in dmso-\(d_6\) and 7b and 8c in dmf-d7.

Fig. S3. ORTEP for the complex cation of \([\text{Cu}_4(\mu-I)_3(\mu-dppm)_2(py)_2]I\) (5).

Fig. S4. ORTEP for the complex cation of \([\text{Cu}_4(\mu-I)_3(\mu-dppm)_2(MesNC)_2]PF_6\) (8b).

Fig. S5. ORTEP for the complex cation of \([\text{Cu}_8(\mu-I)_6(\mu-dppm)_2(BuNC)_2](PF_6)_2\) (9).
Fig. S1. ORTEP for complex [Cu₈(μ-I)₂(μ₃-I)(μ-dpmppm)₂] (1e).

Fig. S2. $^{31}$P{¹H} NMR spectra of (a) 1a, (b) 1b and (c) 2 in dmoso-$d_6$ and (d) 7b and (e) 8c in dmf-$d_7$ at room temperature.
**Fig. S3.** ORTEP for the complex cation of $[\text{Cu}_4(\mu-I)_3(\mu-dpmppm)_2(\text{py})_2]I$ (5).

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**Fig. S4.** ORTEP for the complex cation of $[\text{Cu}_4(\mu-I)_3(\mu-dpmppm)_2(\text{MesNC})_2]PF_6$ (8b).
**Fig. S5.** ORTEP for the complex cation of \([\text{Cu}(\mu-\text{I})_6(\mu-\text{dpmppm})(\text{BuNC})_2](\text{PF}_6)_2\) (9). The terminal isocyanide ligand is disordered in two sites (0.64 and 0.36 occupancies). The thermal ellipsoids of the Cu, I, and P atoms are drawn at the 40% probability level and the N and C atoms are drawn with arbitrary circles for clarity.