Electronic Supplementary Information (ESI)

A new family of one-dimensional bromo-bridged Ir(IV)-Cu(II) complexes based on the hexabromoiridate(IV) metalloligand

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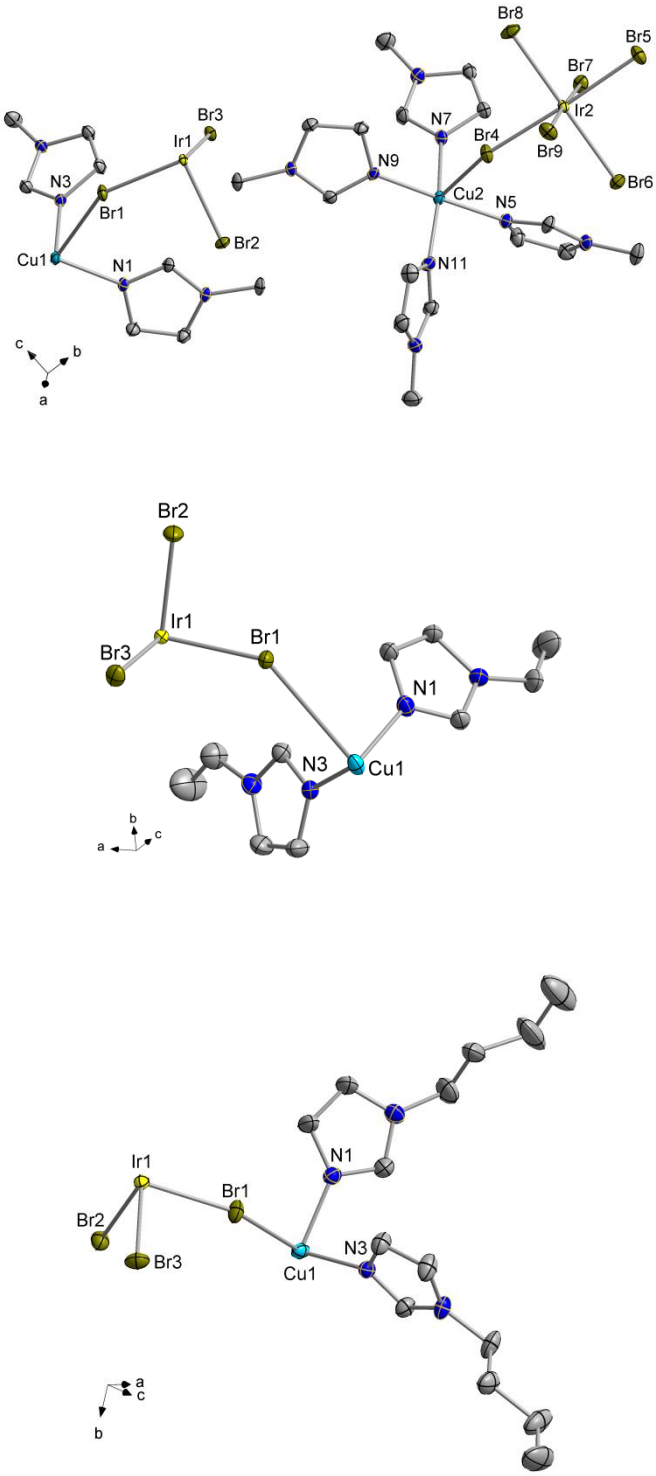
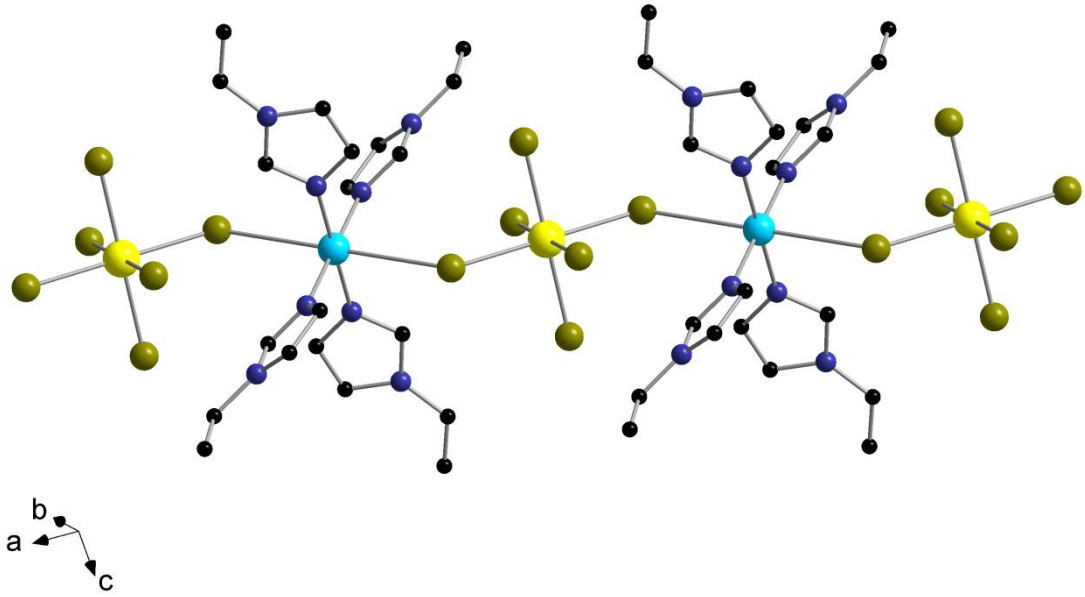


Figure S1. Asymmetric units of compounds **2** (top), **3** (middle) and **4** (bottom). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are depicted at the 50% probability level.

(a)



(b)

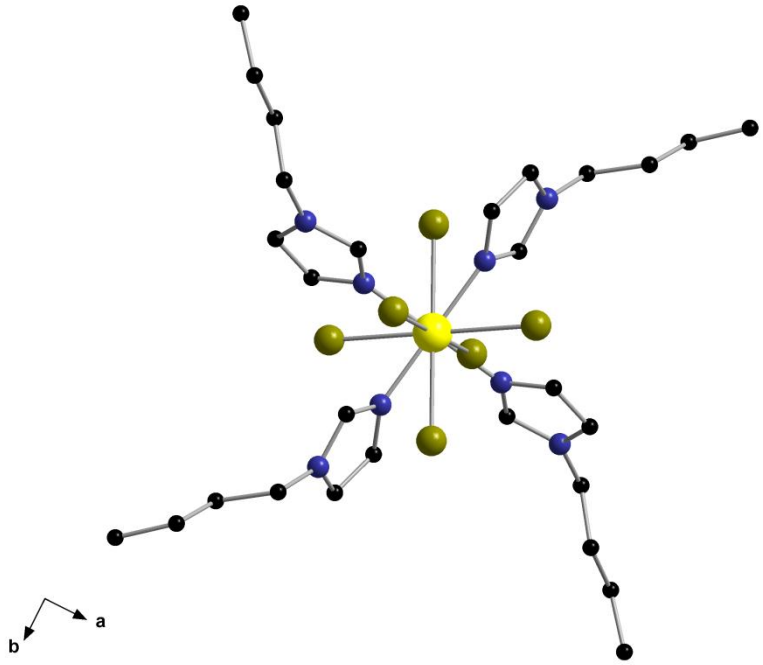


Figure S2. (a) Molecular structure of the one-dimensional motif generated in complex **3**. (b) View along the crystallographic *c* axis of the neutral one-dimensional Ir^{IV}-Cu^{II} complex in **4**. H atoms have been omitted for clarity. Colour code: yellow, Ir; pale blue, Cu; olive green, Br; dark blue, N; black, C.

Table S1. Selected bond lengths (Å) and angles (°) for **2**-**4**.

Compound	**2**	**3**	**4**
Ir(1)-Br(1)	2.4807(4)	2.4855(4)	2.4848(3)
Ir(1)-Br(2)	2.4571(4)	2.4589(4)	2.4736(3)
Ir(1)-Br(3)	2.4819(4)	2.4655(4)	2.4712(3)
Ir(2)-Br(4)	2.4909(5)		
Ir(2)-Br(5)	2.4817(5)		
Ir(2)-Br(6)	2.4699(5)		
Ir(2)-Br(7)	2.4729(5)		
Ir(2)-Br(8)	2.4539(5)		
Ir(2)-Br(9)	2.4801(5)		
Cu(1)-Br(1)	3.1756(5)	3.1239(4)	3.3037(3)
Cu(2)-Br(4)	3.1560(9)		
Cu(2)-Br(5)	3.2903(9)		
Cu(1)-N(1)	1.998(4)	2.026(4)	1.999(3)
Cu(1)-N(3)	2.001(4)	1.986(3)	1.986(2)
Cu(2)-N(5)	1.991(4)		
Cu(2)-N(7)	2.000(4)		
Cu(2)-N(9)	1.980(4)		
Cu(2)-N(11)	1.991(4)		
Br(1)-Ir(1)-Br(2)	89.681(15)	87.644(13)	90.283(10)
Br(1)-Ir(1)-Br(3)	90.580(14)	91.211(13)	90.157(11)
Br(1a)-Ir(1)-Br(2)	90.321(15)	92.357(13)	89.716(10)
Br(1a)-Ir(1)-Br(3)	89.420(14)	88.789(13)	89.843(11)
Br(2)-Ir(1)-Br(3)	89.770(15)	91.745(15)	89.669(11)
Br(2a)-Ir(1)-Br(3)	90.229(15)	88.256(15)	90.331(11)
Br(4)-Ir(2)-Br(5)	176.503(18)		
Br(4)-Ir(2)-Br(6)	91.922(17)		
Br(4)-Ir(2)-Br(7)	89.868(17)		
Br(4)-Ir(2)-Br(8)	89.063(18)		
Br(4)-Ir(2)-Br(9)	90.234(17)		
Br(5)-Ir(2)-Br(6)	90.382(17)		
Br(5)-Ir(2)-Br(9)	92.467(17)		
Br(6)-Ir(2)-Br(7)	89.643(17)		
Br(6)-Ir(2)-Br(8)	177.472(18)		
N(1)-Cu(1)-N(3)	92.00(15)	89.50(14)	88.36(10)
N(1)-Cu(1)-N(3b)	88.00(15)	90.50(14)	91.63(10)
N(5)-Cu(2)-N(9)	178.09(17)		
N(5)-Cu(2)-N(7)	90.60(17)		
N(5)-Cu(2)-N(11)	90.95(17)		
N(7)-Cu(2)-N(9)	88.91(16)		
N(9)-Cu(2)-N(11)	89.88(16)		

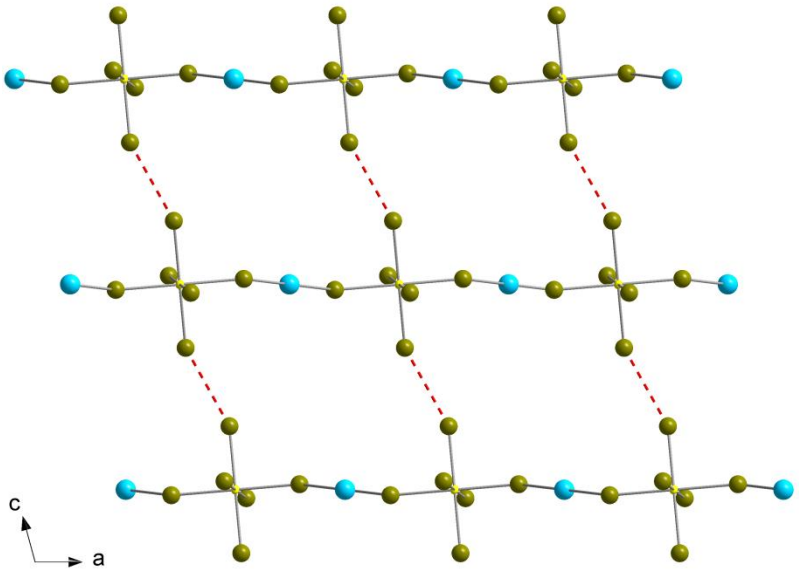


Figure S3. View along the crystallographic *b* axis of the 2D grid of $\{IrBr_5(\mu\text{-}Br)Cu(Viim)_4\}_n$ chains connected through intermolecular Br···Br interactions in the supramolecular 2D assembly in **3** (dashed red lines). Hydrogen atoms and 1-vinylimidazole ligand have been omitted for clarity. Colour code as in Figure S2.

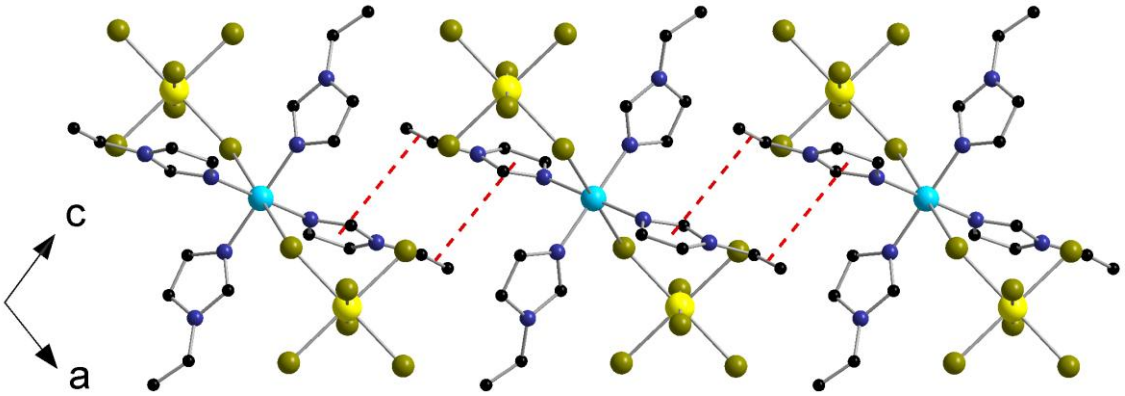


Figure S4. A fragment of the crystal packing of **3** showing the π···π stacking interactions between the vinyl groups and imidazole rings along the crystallographic *b* axis (dashed red lines). Hydrogen atoms have been omitted for clarity. Colour code as in Figure S2.

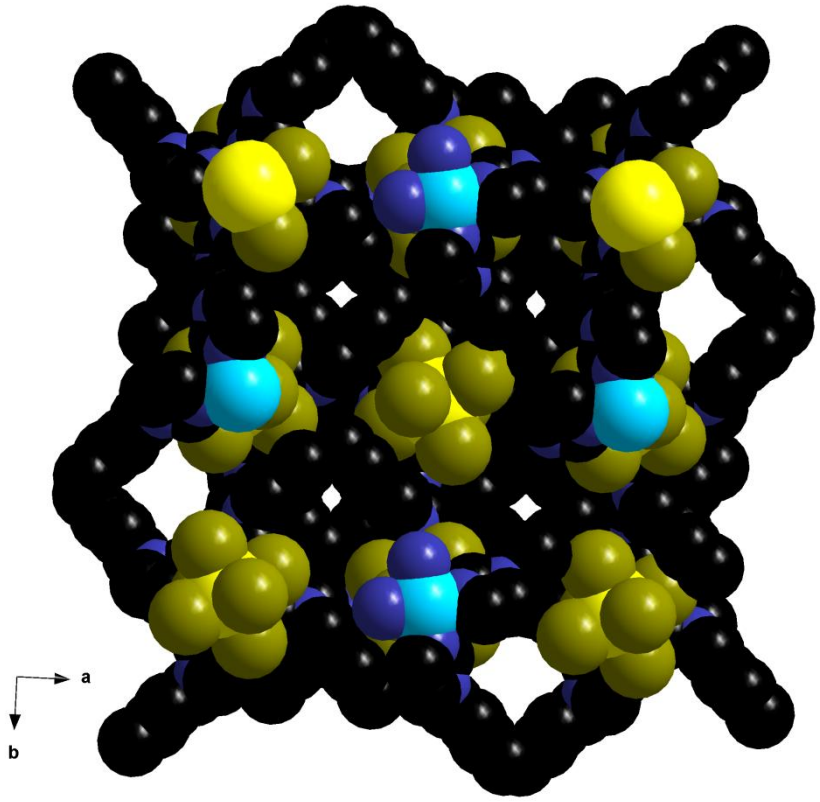


Figure S5. View along the crystallographic *c* axis of a fragment of the crystal packing of **4** highlighting the supramolecular network of adjacent chains as space-filling model. H atoms have been omitted for clarity. Colour code: yellow, Ir; pale blue, Cu; olive green, Br; dark blue, N; black, C.

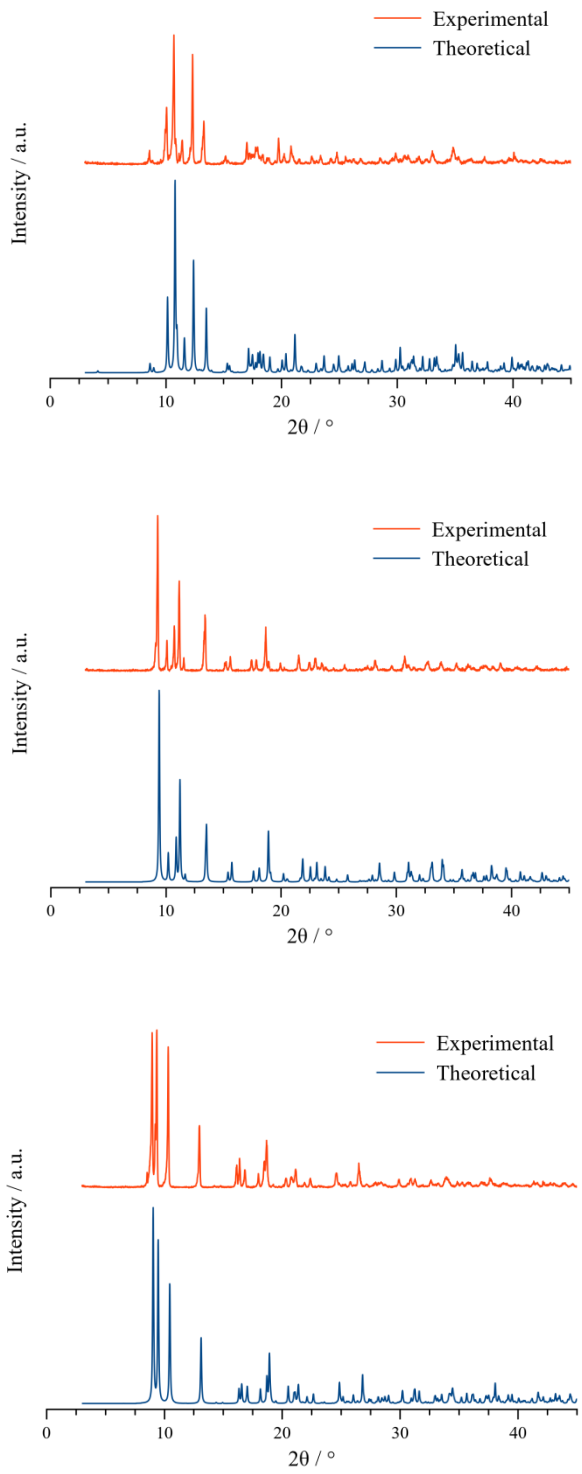


Figure S6. Plot of the theoretical (blue line) and experimental (red line) XRD patterns profile (2θ / °) in the range 3-45° for compounds **2** (top), **3** (middle) and **4** (bottom).

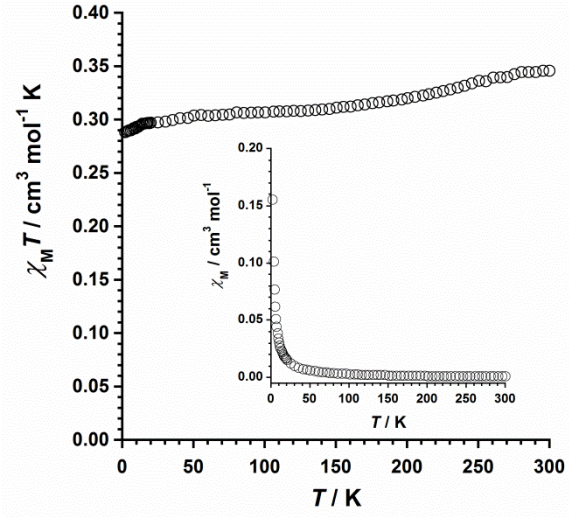


Figure S7. Thermal variation of the $\chi_M T$ product for compound **1**. The inset shows a detail of the thermal variation of the magnetic susceptibility for **1**.

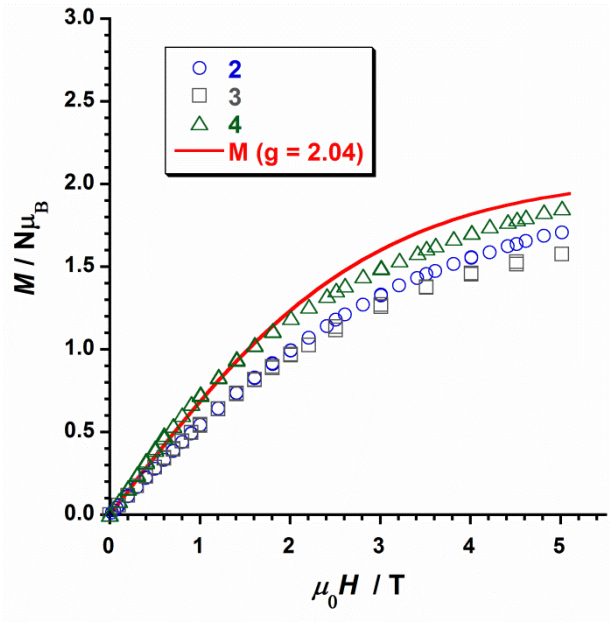


Figure S8. Plot of the variable-field magnetisation *versus* applied field at 2.0 K for compounds **2** (blue circles), **3** (grey squares) and **4** (green triangles). The Brillouin curve (red solid line) was obtained with g = 2.04, a value which is very close to that calculated from the fit of the $\chi_M T$ *versus* T plots.