Supplementary Information B709338A

Crystal-to-crystal transformations in heterometallic yttrium(III)-copper(I) iodide derivatives in a confined solvent-free environment: Influence of solvated yttrium cations on the nuclearity and dimensionality of iodocuprate clusters

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X-Ray structure determination

An abnormally short C---C distance (2.81 Å) for compound **4** is because of the high displacement parameters for carbon atoms C1 and C2 of DMSO group1. The group could not be modelized using a disordered model (i.e. splitting atoms) and was thus constrained to have a geometry close to other DMSO groups. In the structure **5**, the maximum residual density peak Q1 of 13.75 e.Å^{-3} is located at 1.113 Å from H53. Some other high residual densities are: Q2 of 6.93 e.Å^{-3} at 2.261 Å from Cu1 and Q3 of 4.59 e.Å^{-3} at 1.157 Å from Cu1. For compound **6**, the maximum residual density peak Q1 of 5.21 e.Å^{-3} is located at 1.50 Å from Q3. Some other high residual densities are: Q2 of 4.93 e.Å^{-3} at 2.49 Å from I2 and Q3 of 3.56 e.Å^{-3} at 1.50 Å from Q1. These high residual electron densities can be explained by the fact that the cluster condensation is dynamic and occurs over time. Indeed, as the structure is continuously evolving, it was not possible to record data of structures **5** and **6** accurately, especially taking into account the small size of the crystal (0.151 × 0.273 × 0.316). Structures **5** and **6** are accurate (correct distances, thermal ellipsoids) but their data collections are contaminated by metallic fragments that have not yet or already evolved. We thus tried to find a twinning relation in the data but none fitted the observations made. It is also worth noting that evolution is continuing, **6** is not stable but lead to a polycrystalline material.

Table S†1. Selected bond lengths (Å) and angles (°) in **1**

Bond lengths			
Y1–O1	2.340(3)	Cu1–I1	2.507(1)
Y1–O2	2.376(3)	Cu1–I2	2.528(1)
Y1–O3	2.330(3)	Cu1–I3	2.605(9)
Y1–O4	2.358(3)		
Bond angles			
O1–Y1–O2	78.8(1)	O2–Y1–O2^{i}	79.8(2)
O1–Y1–O3	145.0(1)	O2–Y1–O3^{i}	138.4(1)
O1–Y1–O4	111.8(1)	O2–Y1–O4^{i}	72.0(1)
O2–Y1–O3	116.9(1)	O3–Y1–O3^{i}	77.1(2)
O2–Y1–O4	144.2(1)	O3–Y1–O4^{i}	75.7(1)
O3–Y1–O4	74.7(1)	I1–Cu1–I2	124.0(4)
O1–Y1–O1^{i}	142.1(2)	I1–Cu1–I3	120.0(3)
O1–Y1–O2^{i}	72.2(1)	I2–Cu1–I3	116.0(3)
O1–Y1–O3^{i}	71.8(1)	Cu1–I3–Cu^{ii}	180.0
O1–Y1–O4^{i}	80.9(1)		

Symmetry codes: (i) 1-x, y, -1/2-z; (ii) -x, -y, -z.

Table S2. Selected bond lengths (Å) and angles (°) in **2**.

Bond lengths			
Y1–O1	2.356(6)	Cu2–I4	2.644(2)
Y1–O2	2.348(6)	Cu2–I5	2.683(2)
Y1–O3	2.327(6)	Cu3–I3	2.893(2)
Y1–O4	2.299(6)	Cu3–I5	2.961(2)
Y1–O5	2.353(6)	Cu3–I4	2.560(2)
Y1–O6	2.347(6)	Cu3–I6	2.525(2)
Y1–O7	2.408(6)	Cu4–I5	2.596(2)
Y1–O8	2.308(6)	Cu4–I6	2.604(1)
Cu1–I1	2.528(1)	Cu4–I7	2.517(1)
Cu1–I2	2.559(1)	Cu1···Cu2	2.690(2)
Cu1–I3	2.566(1)	Cu2···Cu3	2.469(2)
Cu2–I2	2.551(1)	Cu3···Cu4	2.575(2)
Cu2–I3	2.884(2)		
Bond angles			
I1–Cu1–I2	121.0(5)	O7–Y1–O8	70.9(2)
I1–Cu1–I3	116.1(4)	O3–Y1–O1	134.4(2)
I2–Cu1–I3	122.9(5)	O4–Y1–O1	71.5(2)
I2–Cu2–I3	111.6(6)	O7–Y1–O1	128.9(2)
I2–Cu2–I5	114.3(6)	O8–Y1–O1	76.4(2)
I3–Cu2–I5	98.4(5)	O3–Y1–O5	124.3(2)
I2–Cu2–I4	118.9(6)	O4–Y1–O5	143.8(2)
I3–Cu2–I4	102.1(6)	O7–Y1–O5	135.4(2)
I5–Cu2–I4	108.9(5)	O8–Y1–O5	80.0(2)
I3–Cu3–I5	92.1(5)	O1–Y1–O5	72.5(2)
I3–Cu3–I4	104.0(6)	O3–Y1–O6	78.2(2)

I5–Cu3–I4	103.2(6)	O4–Y1–O6	143.2(2)
I3–Cu3–I6	117.5(7)	O7–Y1–O6	71.4(2)
I5–Cu3–I6	107.7(7)	O8–Y1–O6	84.4(2)
I4–Cu3–I6	126.2(7)	O1–Y1–O6	142.6(2)
I5–Cu4–I6	117.1(5)	O3–Y1–O2	70.6(2)
Cu3–Cu4–I7	153.6(8)	O4–Y1–O2	95.7(2)
I5–Cu4–I7	126.0(6)	O7–Y1–O2	142.7(2)
I6–Cu4–I7	116.0 (6)	O8–Y1–O2	146.4(2)
O3–Y1–O4	79.7(2)	O1–Y1–O2	77.8(2)
O3–Y1–O7	72.2(2)	O5–Y1–O6	72.7(2)
O4–Y1–O7	74.1(2)	O5–Y1–O2	72.0(2)
O3–Y1–O8	142.6(2)	O6–Y1–O2	104.1(2)
O4–Y1–O8	96.0(2)		

Table S3. Selected bond lengths (Å) and angles (°) in **3**.

Bond lengths			
Y1–O1	2.358(1)	Y1–O7	2.313(1)
Y1–O2	2.388(1)	Y1–O8	2.329(1)
Y1–O3	2.268(1)	Cu1–I1	2.565(2)
Y1–O4	2.325(1)	Cu1–I2	2.535(3)
Y1–O5	2.401(1)	Cu1–I3	2.547(2)
Y1–O6	2.315(1)		
Bond angles			
O1–Y1–O2	72.2(4)	O3–Y1–O7	97.3(5)
O1–Y1–O3	77.1(5)	O3–Y1–O8	144.7(4)
O1–Y1–O4	71.1(4)	O4–Y1–O5	75.9(5)
O1–Y1–O5	136.0(4)	O4–Y1–O6	80.1(5)
O1–Y1–O6	129.1(5)	O4–Y1–O7	146.2(5)
O1–Y1–O7	142.7(5)	O4–Y1–O8	101.3(5)
O1–Y1–O8	74.4(4)	O5–Y1–O6	70.4(4)
O2–Y1–O3	75.6(5)	O5–Y1–O7	73.9(5)
O2–Y1–O4	142.4(4)	O5–Y1–O8	141.5(4)
O2–Y1–O5	129.0(4)	O6–Y1–O7	75.7(6)
O2–Y1–O6	131.2(5)	O6–Y1–O8	71.2(4)
O2–Y1–O7	70.7(5)	O7–Y1–O8	93.0(4)
O2–Y1–O8	76.2(4)	I1–Cu1–I2	119.6(1)
O3–Y1–O4	88.5(5)	I1–Cu1–I3	118.8(9)
O3–Y1–O5	73.8(4)	I2–Cu1–I3	121.5(9)
O3–Y1–O6	144.1(4)		

Table S4. Selected bond lengths (Å) and angles (°) in **4**.

Bond lengths			
Y1–O1	2.294(8)	Y1–O7	2.420(7)
Y1–O2	2.381(8)	Y1–O8	2.371(8)
Y1–O3	2.373(8)	Cu1–I1	2.532(2)
Y1–O4	2.311(7)	Cu1–I2	2.549(2)
Y1–O5	2.313(7)	Cu1–I3	2.526(2)
Y1–O6	2.343(7)		
Bond angles			
O1–Y1–O2	77.7(3)	O3–Y1–O7	138.9(3)
O1–Y1–O3	74.7(3)	O3–Y1–O8	142.3(3)
O1–Y1–O4	146.5(3)	O4–Y1–O5	80.8(3)
O1–Y1–O5	106.3(3)	O4–Y1–O6	137.3(3)
O1–Y1–O6	74.8(3)	O4–Y1–O7	68.1(3)
O1–Y1–O7	144.9(3)	O4–Y1–O8	111.2(3)
O1–Y1–O8	84.1(4)	O5–Y1–O6	73.6(3)
O2–Y1–O3	73.7(3)	O5–Y1–O7	80.1(3)
O2–Y1–O4	79.3(3)	O5–Y1–O8	141.2(3)
O2–Y1–O5	146.8(3)	O6–Y1–O7	74.2(3)
O2–Y1–O6	137.1(3)	O6–Y1–O8	73.5(3)
O2–Y1–O7	115.9(3)	O7–Y1–O8	71.6(3)
O2–Y1–O8	71.5(3)	I1–Cu1–I2	118.6(7)
O3–Y1–O4	75.5(3)	I1–Cu1–I3	121.6(7)
O3–Y1–O5	75.7(3)	I2–Cu1–I3	119.7(7)
O3–Y1–O6	127.8(3)		

Table S5. Selected bond lengths (Å) and angles (°) in **5**.

Bond lengths			
Y1–O1	2.420(2)	Cu4–I10^{i}	2.608(5)
Y1–O2	2.410(2)	Cu5–I4	2.676(5)
Y1–O3	2.289(2)	Cu5–I7	2.673(5)
Y1–O4	2.310(2)	Cu5–I8	2.603(5)
Y1–O5	2.320(2)	Cu5–I9	2.729(5)
Y1–O6	2.290(2)	Cu6–I5	2.697(6)
Y1–O7	2.390(2)	Cu6–I6	2.744(6)
Y1–O8	2.249(2)	Cu6–I8^{ii}	2.593(5)
Cu1–I1	2.536(6)	Cu6–I9	2.635(5)
Cu1–I2	2.583(7)	Cu7–I6	2.751(5)
Cu1–I3	2.550(6)	Cu7–I7	2.640(5)
Cu2–I2	2.618(5)	Cu7–I9	2.668(5)
Cu2–I4	2.693(5)	Cu7–I10	2.592(5)
Cu2–I5	2.648(5)	Cu2···Cu3	2.826(6)
Cu2–I6	2.731(5)	Cu2···Cu4	3.030(7)
Cu3–I3	2.614(5)	Cu2···Cu6	3.201(7)
Cu3–I4	2.699(5)	Cu3···Cu5	3.035(6)
Cu3–I6	2.737(5)	Cu3···Cu7	3.112(7)
Cu3–I7	2.609(5)	Cu4···Cu5	2.860(6)
Cu4–I4	2.672(5)	Cu4···Cu6	3.045(7)
Cu4–I5	2.708(5)	Cu7···Cu6	2.930(7)
Cu4–I9	2.696(5)		

Bond angles			
O5–Y1–O1	67.7(7)	I4–Cu2–I2	106.4(2)
O2–Y1–O1	135.9(7)	I5–Cu2–I4	107.5(2)
O5–Y1–O2	79.6(7)	I6–Cu2–I4	113.1(2)
O5–Y1–O3	89.7(3)	I5–Cu2–I6	103.1(2)
O2–Y1–O3	69.5(7)	I6–Cu3–I3	109.0(2)
O1–Y1–O3	81.2(8)	I7–Cu3–I3	111.2(2)
O5–Y1–O4	134.1(7)	I4–Cu3–I3	110.5(2)
O2–Y1–O4	130.4(6)	I6–Cu3–I4	112.8(2)
O1–Y1–O4	67.3(6)	I7–Cu3–I4	107.4(2)
O3–Y1–O4	75.0(7)	I6–Cu3–I7	105.8(2)
O8–Y1–O4	73.4(6)	I5–Cu4–I4	106.4(2)
O5–Y1–O6	101.0(6)	I9–Cu4–I4	112.6(2)
O2–Y1–O6	137.9(7)	$I10^{i}$–Cu4–I4	111.9(2)
O1–Y1–O6	78.9(9)	I5–Cu4–I9	106.9(2)
O3–Y1–O6	151.7(6)	I5–Cu4–$I10^{i}$	109.4(2)
O8–Y1–O6	87.4(8)	I9–Cu4–$I10^{i}$	109.3(2)
O4–Y1–O6	78.8(6)	I9–Cu5–I4	111.4(2)
O7–Y1–O6	70.7(6)	I7–Cu5–I4	106.2(2)
O5–Y1–O7	75.7(6)	I9–Cu5–I7	103.3(2)
O2–Y1–O7	68.7(6)	I7–Cu5–I8	111.0(2)
O1–Y1–O7	126.2(6)	I4–Cu5–I8	112.4(2)
O3–Y1–O7	137.6(6)	I9–Cu5–I8	112.1(2)
O8–Y1–O7	82.3(6)	I5–Cu6–I6	101.5(2)
O4–Y1–O7	141.7(8)	I9–Cu6–I6	110.2(2)
O5–Y1–O8	152.1(6)	$I8^{ii}$–Cu6–I6	109.2(2)
O2–Y1–O8	76.6(6)	I5–Cu6–I9	109.1(2)
O1–Y1–O8	140.1(6)	I5–Cu6–$I8^{ii}$	112.8(2)
O3–Y1–O8	95.3(7)	I9–Cu6–$I8^{ii}$	113.3(2)
I2–Cu1–I1	123.3(2)	I9–Cu7–I6	109.1(2)
I3–Cu1–I1	117.7(2)	I9–Cu7–I7	105.9(2)
I3–Cu1–I2	116.8(2)	I6–Cu7–I7	104.5(2)
I5–Cu2–I2	115.8(2)	I6–Cu7–I10	112.9(2)
I6–Cu2–I2	111.0(2)	I7–Cu7–I10	109.9(2)

Symmetry codes: (i) $-x+1, y-1/2, -z+3/2$; (ii) $-x+1, y+1/2, -z+3/2$.

Table S6. Selected bond lengths (Å) and angles (°) in **6**.

Bond lengths			
Y1–$O1w^{iv}$	2.520(2)	Cu1–I2	2.701(2)
Y1–$O1w^{v}$	2.520(2)	Cu1–$I2^{ii}$	2.672(2)
Y1–$O2^{iv}$	2.342(2)	Cu1–I3	2.645(2)
Y1–$O2^{v}$	2.342(2)	Cu2–I2	2.720(2)
Y1–$O2^{iii}$	2.342(2)	Cu2–I3	2.608(2)
Y1–$O2^{vi}$	2.342(2)	Cu2–$I2^{iii}$	2.720(2)
Y1–$O2^{vii}$	2.342(2)	Cu2–$I3^{iii}$	2.608(2)
Y1–O1w	2.520(2)	Cu1···$Cu1^{i}$	2.795(3)
Y1–O2	2.342(2)	Cu1···$Cu1^{ii}$	2.795(3)
Cu1–I1	2.657(3)	Cu1···Cu2	2.775(2)
Bond angles			

O1w^{iv}–Y1–O1w^{v}	120.0(5)	O1w^{iv}–Y1–O2	65.2(4)
O1w^{iv}–Y1–O2^{iv}	73.5(4)	O1w^{v}–Y1–O2	134.7(4)
O1w^{v}–Y1–O2^{iv}	65.2(4)	O2^{iv}–Y1–O2	75.5(6)
O1w^{iv}–Y1–O2^{v}	134.7(4)	O2^{v}–Y1–O2	75.5(6)
O1w^{v}–Y1–O2^{v}	73.5(4)	O2^{iii}–Y1–O2	147.0(9)
O2^{iv}–Y1–O2^{v}	75.5(6)	O2^{vi}–Y1–O2^{vii}	75.5(6)
O1w^{iv}–Y1–O2^{iii}	134.7(4)	O2^{vi}–Y1–O1w	65.2(4)
O1w^{v}–Y1–O2^{iii}	65.2(4)	O2^{vii}–Y1–O1w	134.7(4)
O2^{iv}–Y1–O2^{iii}	130.5(8)	O2^{vi}–Y1–O2	90.7(8)
O2^{v}–Y1–O2^{iii}	90.7(8)	O2^{vii}–Y1–O2	130.5(8)
O1w^{iv}–Y1–O2^{vi}	73.5(4)	O1w–Y1–O2	73.5(4)
O1w^{v}–Y1–O2^{vi}	134.7(4)	I2^{ii}–Cu1–I1	112.5(8)
O2^{iv}–Y1–O2^{vi}	147.0(9)	I2^{ii}–Cu1–I2	107.6(1)
O2^{v}–Y1–O2^{vi}	130.5(8)	I1–Cu1–I2	111.5(8)
O2^{iii}–Y1–O2^{vi}	75.5(6)	I2^{ii}–Cu1–I3	107.1(8)
O1w^{iv}–Y1–O2^{vii}	65.2(4)	I1–Cu1–I3	105.6(9)
O1w^{v}–Y1–O2^{vii}	73.5(4)	I2–Cu1–I3	112.4(8)
O2^{iv}–Y1–O2^{vii}	90.7(8)	I2^{iii}–Cu2–Cu1^{iii}	58.9(5)
O2^{v}–Y1–O2^{vii}	147.0(9)	I2^{iii}–Cu2–Cu1	134.6(9)
O2^{iii}–Y1–O2^{vii}	75.5(6)	I2^{iii}–Cu2–I3^{iii}	113.0(4)
O1w^{iv}–Y1–O1w	120.0(5)	I2^{iii}–Cu2–I2	98.4(11)
O1w^{v}–Y1–O1w	120.0(1)	I2^{iii}–Cu2–I3	108.2(4)
O2^{iv}–Y1–O1w	134.7(4)	I3^{iii}–Cu2–I3	115.0(1)
O2^{v}–Y1–O1w	65.2(4)	I2–Cu2–I3	113.0(4)
O2^{iii}–Y1–O1w	73.5(4)		

Symmetry codes: (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$; (iii) $-x+4/3, -x+y+2/3, -z+1/6$; (iv) $-x+y, -x+2, z$; (v) $-y+2, x-y+2, z$; (vi) $y-2/3, x+2/3, -z+1/6$; (vii) $x-y+4/3, -y+8/3, -z+1/6$.

Table S7. Selected TG-DTA-MS data for **1**-**6**.

	1	**2**	**3**	**4**	**5**	**6**
Decomposition Temp. (°C)	300	450	350	500	450	450
Total weight loss (%)	62.6	41.8	63.2	56.4	38.8	39.0
Endothermic peaks (°C)	51, 115, 165, 200, 374	85, 120, 258, 320, 372, 408	122, 190, 253, 280, 374	102, 116, 128, 164, 188, 216, 242, 374, 459	102, 125, 258, 372, 408	85, 113, 238, 372, 408
Exothermic peaks (°C)	264	-	-	-	-	-
Range of temp. for loss of HI in MS (°C)	160-300	285-460	177-348	173-365	290-445	280-458

Table S8. Mulliken and Hirshfeld charges calculated for **1**-**6**.

	Cu	I	Y
Mulliken charges			
$[Y(DMSO)_8][Cu_2I_5]$ (**1**)	-0.24, -0.25	-0.35 to -0.39 (terminal) -0.02 (bridging)	2.32
$[Y(DMSO)_6(DMF)_2][CuI_3][I]$ (**3**)	-0.41	0.11 to 0.36 (for $[CuI_3]^{2-}$) -0.04 (for $[I]^-$)	2.15
$[Y(DMSO)_6(H_2O)_2]$ $[CuI_3][I]$ (**4**)	-1.15	0.01 to 0.06 (for $[CuI_3]^{2-}$) -0.64 (for $[I]^-$)	2.26
$[Cu_4I_7]^{3-}$ of (**2**)	-0.15 to -0.19	-0.10 to -0.60	-
$[Cu_7I_{12}]^{5-}$ of (**5**)	-0.19 to -0.25	0.10 to -0.68	-
$[Cu_6I_{13}]^{6-}$ of (**6**)	0.02 to -0.23	-0.12 to -0.75	-
Hirshfeld charges			
$[Y(DMSO)_8][Cu_2I_5]$ (**1**)	0.06, 0.07	-0.37 to -0.40 (terminal) -0.23 (bridging)	0.48
$[Y(DMSO)_6(DMF)_2][CuI_3][I]$ (**3**)	0.20	-0.05 to 0.15	0.54
$[Y(DMSO)_6(H_2O)_2][CuI_3][I]$ (**4**)	0.02	-0.42 to -0.48 (for $[CuI_3]^{2-}$) -0.54 (for $[I]^-$)	0.50
$[Cu_4I_7]^{3-}$ of (**2**)	0.01	-0.28 to -0.62	-
$[Cu_7I_{12}]^{5-}$ of (**5**)	-0.04 to 0.02	-0.13 to -0.66	-
$[Cu_6I_{13}]^{6-}$ of (**6**)	-0.07 to -0.08	-0.10 to -0.74	-

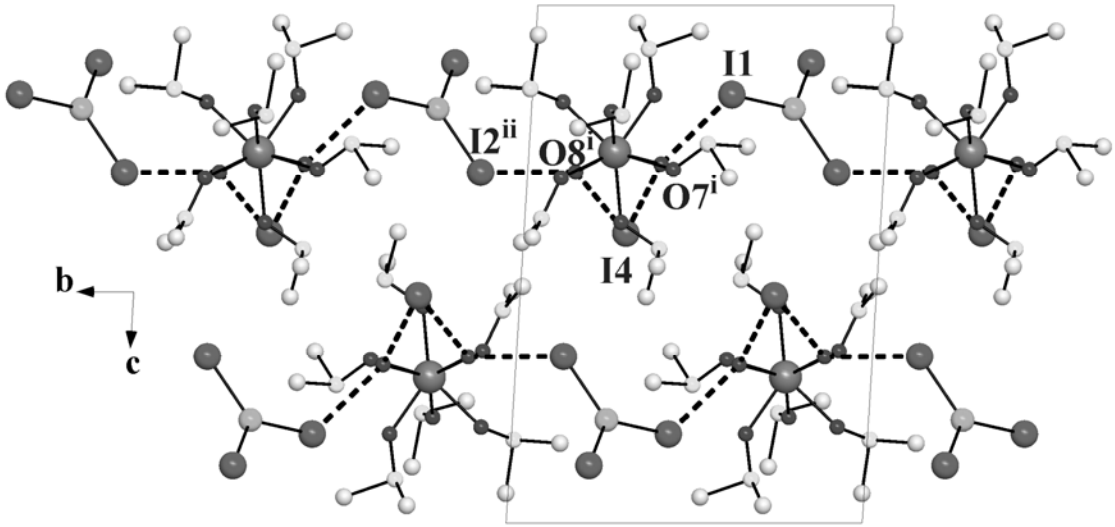


Figure S1: H-bonding between water molecules and iodides in **4**: $O7^{i}\cdots I1$ 3.57(8), $O7^{i}\cdots I4$ 3.48(7), $O8^{i}\cdots I4$ 3.49(8), $O8^{i}\cdots I2^{ii}$ 3.42(8) Å, symmetry codes: (i) -1 + *x*, *y*, *z*; (ii) *x*, -1+ *y*, *z*.

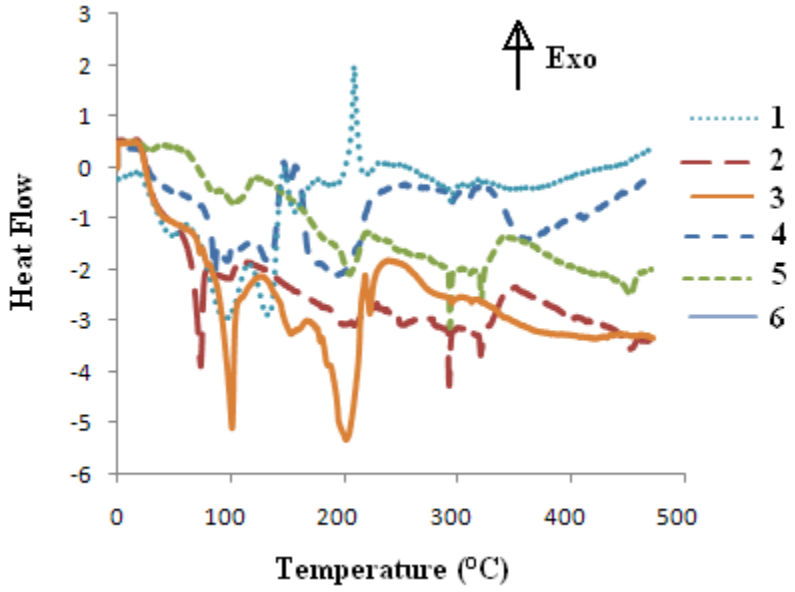
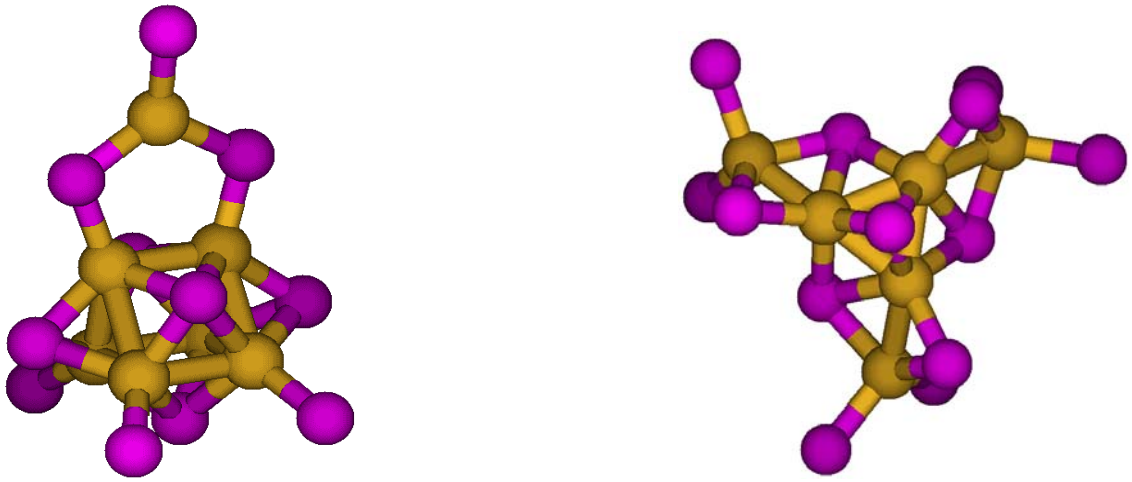


Figure S2: DTA curve of **1-6**.



(a) (b)

Figure S3. Ball and stick representation of $[Cu^{I}_{7}I_{12}]^{-5}$ (a) and $[Cu^{I}_{5}Cu^{II}I_{13}]^{-6}$ (b) models used for theoretical calculations of 1D and 2D copper iodide clusters in (**5**) in (**6**), respectively. Atom color designations: copper (brown) and iodine (violet)