

**Electronic Supporting Information**

**Halogen Bonding between Metal-bound  $I_3^-$  and Unbound  $I_2$ : The Trapped  $I_2 \cdots I_3^-$  Intermediate in the Controlled Assembly of Copper(I)-based Polyiodides**

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## S1. X-ray diffraction studies

**Table S1.** Crystal data and structure refinement for **1**, **2<sup>I</sup>**, **2·½I<sub>2</sub>**, and **3**.

Identification code	<b>1</b>	<b>2<sup>I</sup></b>	<b>2·½I<sub>2</sub></b>	<b>3</b>
Empirical formula	C <sub>27</sub> H <sub>27</sub> CuIN <sub>3</sub>	C <sub>27</sub> H <sub>27</sub> CuI <sub>3</sub> N <sub>3</sub>	C <sub>27</sub> H <sub>27</sub> CuI <sub>4</sub> N <sub>3</sub>	C <sub>27</sub> H <sub>27</sub> CuI <sub>5</sub> N <sub>3</sub>
Formula weight	583.95	837.75	964.65	1091.55
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	C2/m
a/Å	10.4150(2)	8.2477(2)	7.4862(2)	20.6771(6)
b/Å	21.6264(5)	16.9484(4)	10.8376(4)	6.84507(19)
c/Å	22.6885(5)	21.8622(5)	20.8257(7)	25.8808(9)
α/°	92.433(2)	105.864(2)	99.148(3)	90
β/°	95.552(2)	92.8304(19)	94.089(3)	114.426(4)
γ/°	95.644(2)	98.7447(19)	106.371(3)	90
Volume/Å <sup>3</sup>	5054.73(19)	2892.12(12)	1588.45(9)	3335.2(2)
Z	8	4	2	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.535	1.924	2.017	2.174
μ/mm <sup>-1</sup>	2.104	3.977	4.594	5.303
F(000)	2336.0	1592.0	902.0	2016.0
Crystal size/mm <sup>3</sup>	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.15	0.12 × 0.1 × 0.04	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.186 to 55	5.216 to 55	6.15 to 54.998	6.326 to 54.994
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 28, -29 ≤ l ≤ 28	-10 ≤ h ≤ 10, -22 ≤ k ≤ 22, -28 ≤ l ≤ 28	-9 ≤ h ≤ 9, -14 ≤ k ≤ 13, -27 ≤ l ≤ 26	-26 ≤ h ≤ 26, -8 ≤ k ≤ 8, -33 ≤ l ≤ 33
Reflections collected	49870	31020	16768	14047
Independent reflections	23213 [R <sub>int</sub> = 0.0310, R <sub>sigma</sub> =	13260 [R <sub>int</sub> = 0.0234,	7115 [R <sub>int</sub> = 0.0319,	4126 [R <sub>int</sub> = 0.0212, R <sub>sigma</sub> =

	0.0448]	$R_{\text{sigma}} = 0.0322]$	$R_{\text{sigma}} = 0.0420]$	0.0214]
Data/restraints/parameters	23213/0/1177	13260/0/625	7115/0/322	4126/0/223
Goodness-of-fit on $F^2$	1.027	1.116	1.068	1.358
Final R indexes [ $I >= 2\sigma (I)$ ]	$R_1 = 0.0301$ , $wR_2 = 0.0625$	$R_1 = 0.0273$ , $wR_2 = 0.0509$	$R_1 = 0.0300$ , $wR_2 = 0.0604$	$R_1 = 0.0323$ , $wR_2 = 0.0605$
Final R indexes [all data]	$R_1 = 0.0406$ , $wR_2 = 0.0672$	$R_1 = 0.0349$ , $wR_2 = 0.0538$	$R_1 = 0.0441$ , $wR_2 = 0.0681$	$R_1 = 0.0350$ , $wR_2 = 0.0612$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.75/-0.56	0.67/-0.61	1.19/-0.85	1.11/-1.45
CCDC number	2211056	2211053	2211054	2211055

**Table S2.** Structural parameters of the studied crystals.

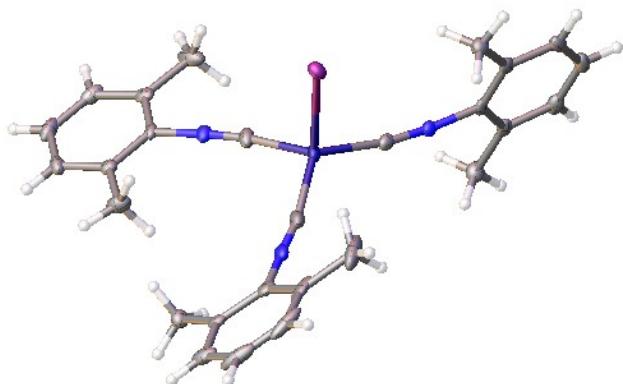
	<b>1</b>	<b>2<sup>I</sup></b>	<b>2<sup>II</sup></b>	<b>2·½I<sub>2</sub></b>	<b>3</b>
$d(\text{Cu}-\text{I})$ , Å	2.6841(5)–2.7004(6)	2.7222(4) and 2.7217(4)	2.8444(6)	2.9015(7)	3.42515(11) semicoordination bond
$\Sigma(\angle \text{C}-\text{Cu}-\text{C})$ , °	343–346	337 and 341	353	354	360
$d(\text{I}_{\text{Cu}}-\text{I})$ , Å	–	3.0441(6) 3.0640(6) covalent bond in $\text{I}_3^-$	2.9677(6) covalent bond in $\text{I}_3^-$	3.0520(5) covalent bond in $\text{I}_3^-$	3.0836(6) covalent bond in $\text{I}_5^-$
$d(\text{Cu} \cdots \text{I})$ , Å		–	3.9988(6) Cu···I <sup>2</sup> weak semicoordination bond	3.9387(6) Cu···I <sup>2</sup> weak semicoordination bond	3.42515(11) semicoordination bond
$d(\text{I}^3 \cdots \text{I}^3)$ , Å		3.6519(7) and 4.1002(7) Type-I halogen···halogen interaction	–	3.5172(8) Type-I halogen···halogen interaction	4.3538(11)
$d(\text{I}_{\text{Cu}} \cdots \text{I})$ , Å	–	–	–	3.3658(6) $\text{I}_2 \cdots \text{I}_3^-$ HaB	3.1105(8) covalent bond in $\text{I}_5^-$

## S2. Structural features

**S2.1. Copper(I)-based iodides and polyiodides: brief overview.** Copper complexes (first of all, Cu<sup>II</sup> species) demonstrate very rich and versatile polyiodide chemistry, reviewed in ref.<sup>1</sup>, while copper(I) polyiodides are far less studied. (Polyiodide)Cu<sup>I</sup> species are mostly represented by triiodides and supporting organic ligands in these systems conventionally include *N*- and *S*-coordinated mono- and bidentate species. Thus, the dicopper(I) adduct  $[\text{Cu}_2(\mu_4\text{-L})(\mu_2\text{-I})(\text{I}_2)(\text{I}_3)]_n \cdot n\text{I}_2$  (*L* = 1-tetrazole-4-imidazole-benzene) forms 3D-network built by 1D coordination polymer chains; these chains in turn are linked by I<sub>2</sub> via HaB.<sup>2</sup> Other examples of copper(I)- and also mixed-valent copper(I/II) species include the binuclear  $[\text{Cu}_2\text{I}_2(\text{ttab})]$  (ttab = 1,2,4,5-tetra(7-azaindo-yl)benzene),<sup>3</sup>  $[\text{Cu}_2(\text{I}_3)_2(\text{ttab})]$ ,<sup>3</sup> the trinuclear  $[\text{Cu}_3(\mu\text{-I})_2(\kappa^1\text{-I}_3)_2(\text{L}')_2]_n$  (*L'* = 1-(4,5-dihydro-3-propyl-imidazolidin-2-yl)-3-propyl-imidazolidine-2-thione),<sup>4</sup> and the heterometallic  $[\text{Mo}_2\text{O}_2\text{S}_6\text{Cu}_6(\mu\text{-I}_2)(4,4'\text{-bipy})_3]_n \cdot n\text{H}_2\text{O}$  compounds.<sup>5</sup> The XRD structures of metal-organic frameworks such as  $[\text{Cu}(\mu_2(\text{I}^1,\text{I}^3)\text{-I}_3)\{\mu_2\text{-(3,3',5,5'-tetramethyl-4,4'-bipyrazole)}\}]_n$ ,  $[\text{Cu}(\mu_2(\text{I}^1,\text{I}^1)\text{-I}_3)\{\mu_2\text{-(3,3',5,5'-tetramethyl-4,4'-bipyrazole)}\}]_n$ , and  $[\text{Cu}(\mu_2(\text{I}^1,\text{I}^1)\text{-I}_2\text{Cl})\{\mu_2\text{-(3,3',5,5'-tetramethyl-4,4'-bipyrazole)}\}]_n$ , revealed that I<sub>2</sub> or ICl molecules are halogen-bonded to the iodide ligand in the I-[Cu<sup>I</sup>] moiety.<sup>6</sup> Notably in the context of this study, although isocyanide ligands typically stabilize low oxidation state metal ions<sup>7</sup> (including copper(I)<sup>8</sup>), (RNC)Cu<sup>I</sup>-based polyhalides are yet unreported.

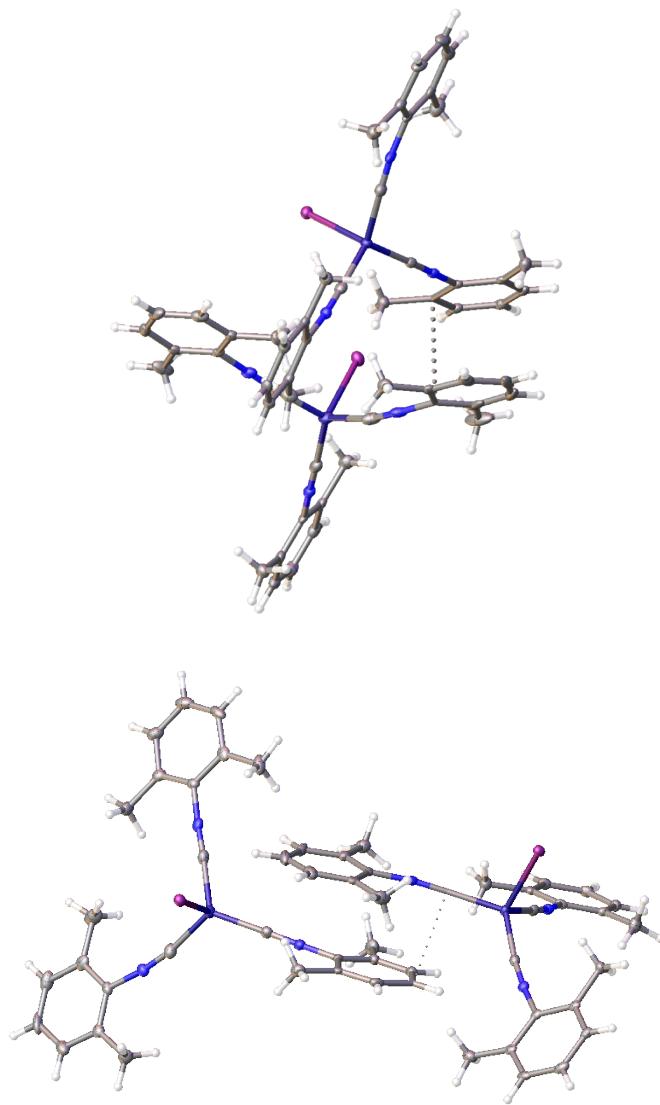
**S2.2. The XRD structure of 1.** The XRD structure of **1** (Figure S1) is analogous to those of the previously reported complexes, namely  $[\text{CuI}(\text{CNR})_3]$  (*R* = C<sub>6</sub>H<sub>4</sub>-4-Me, CSD code is GELNIU<sup>9</sup> and C<sub>6</sub>H<sub>3</sub>(2,6-Mes)<sub>2</sub> WOJQES<sup>10</sup>). The coordination polyhedra of these complexes are formed by the three isocyanide ligands and one iodide resulting in a distorted tetrahedral geometry (geometry index  $\tau_4$  = 0.87–0.94<sup>11</sup>). The crystal structure of **1** (Figure S1) is composed by four independent molecules of  $[\text{CuI}(\text{CNXyl})_3]$ . The coordination polyhedron is formed by the three

isocyanide ligands and one iodide resulting in a distorted tetrahedral geometry (geometry index  $\tau_4$  = 0.87–0.94<sup>11</sup>). The bond angles around the copper(I) center spans the interval from 99.87(8) to 122.35(12)°, which is similar to that in  $[\text{CuI}(\text{CNR})_3]$  ( $\text{R} = \text{C}_6\text{H}_4\text{Me}-4$  100.3(9)–117.2(4)° CSD refcode GELNIU;<sup>9</sup>  $\text{C}_6\text{H}_3(\text{Mes})_2-2,6$  100.02(8)–117.18(11)° WOJQES<sup>10</sup>). The Cu–I (2.6841(5)–2.7004(6) Å) and Cu–C bond lengths (1.927(2)–1.941(3) Å) are comparable with those observed in GELNIU<sup>9</sup> and WOJQES.<sup>10</sup> The fragments Cu–C–N (169.2(3)–177.1(2)°) deviate from the linearity.



**Figure S1.** View of the molecular structure of **1**.

We detected the  $\pi$ – $\pi$  stacking (**Figure S2**) in the crystal packing occurred between the arene rings of the neighboring complexes (interplane distance ca. 3.4 Å) and contacts between the arene ring and  $\pi$ -system of the isocyanide CN ( $\text{C}\cdots\text{C} = 3.282(4)$ – $3.655(4)$  Å). The latter contact apparently reflects the interaction between the electrophilic region ( $\pi$ -hole) of the isocyanide group and  $\pi$ -electron density of the aromatic ring. Similar ( $\pi$ -hole)- $\pi$  interactions have been previously reported for  $(\text{ArNC})\text{Pd}^{\text{II}}$  complexes.<sup>12</sup> No other significant structure-directing noncovalent interactions were identified.



**Figure S2.** The stacking interactions (dotted line) in the structure of **1**.

**S2.3. The XRD structures of  $2^{\text{I}}$  and  $2^{\text{II}}$ .** The structure of  $2^{\text{I}}$  contains two types of symmetrically independent molecules of  $[\text{Cu}(\text{I}_3)(\text{CNXyl})_3]$  and the copper(I) center exhibits a distorted tetrahedral environment ( $\tau_4 = 0.93\text{--}0.95^{11}$ ) with  $\angle(\text{I}-\text{Cu}-\text{C}) 101.77(10)\text{--}109.69(10)^\circ$  and  $\angle(\text{C}-\text{Cu}-\text{C}) 110.80(13)\text{--}115.82(13)^\circ$  (**Figure 2**). The Cu–I and covalent I–I bonds within the  $\text{I}_3^-$  ligand are usual. The Cu–I distances are 2.7222(4) and 2.7217(4) Å, and these values are slightly higher than the C–I distance in **1** (2.6841(5)–2.7004(6) Å) and longer than the C–I distance (2.6976(18) Å) in a four-coordinated Cu<sup>I</sup> center (RIQSUI,  $\text{I}_3^-$  ligand at  $\{\text{CuN}_2\text{I}_2\}$  metal centers bearing coordinated terminal  $\text{I}_3^-$ ).<sup>2</sup> The triiodide ligand is slightly deviated from the  $\text{Cu}(\text{CNXyl})_3$  moiety with  $\angle(\text{I}2-\text{I}1-\text{Cu}1) 93.966(15)$  and  $91.362(14)^\circ$ ; the I<sub>3</sub> linkage is nearly linear ( $\angle(\text{I}3-\text{I}2-$

I1) 176.591(11) and 176.119(10) $^{\circ}$ ). The bonds within the  $\text{I}_3^-$  ligand (I1–I2 2.8035(6) and 2.8100(6), and I2–I3 3.0640(6) and 3.0441(6)  $\text{\AA}$ ) are usual for the terminal metal-bound triiodides.<sup>3-4</sup> Other bonds and angles of the isocyanide ligands are similar, within  $3\sigma$ , to those in the structure of **1**.

We also observed short I3…I3 contact occurred between two molecules of **2<sup>I</sup>** and we attributed this linkage to Type-I halogen-halogen interactions<sup>13</sup> (I3…I3 3.6519(7)  $\text{\AA}$  and  $\angle(\text{I2–I3…I3})$  141.87(2) $^{\circ}$ ).

Main parameters, bond lengths and angles of **2<sup>II</sup>** are quite similar to those found for **2<sup>I</sup>**. Contacts I…I were not observed for **2<sup>II</sup>**, but we identified short Cu…I contact (3.9988(6)  $\text{\AA}$ ). These two polymorphs are also different by the mutual arrangement of molecules in structures: head-to-head for **2<sup>I</sup>** and head-to-tail for **2<sup>II</sup>** (**Figure 2**).

Examination of the structural changes on going from **1** to **2** (**Scheme 1**) indicates that the  $d(\text{Cu–I})$  distance is slightly elongated (by 0.03–0.04  $\text{\AA}$  for **2<sup>I</sup>**; 0.14–0.16  $\text{\AA}$  for **2<sup>II</sup>**). The coordination polyhedron in **2<sup>I</sup>** remains the same and only the  $\Delta\mathcal{Z}(\angle\text{C–Cu–C})$  is decreased by 2–9 $^{\circ}$ , while the coordination polyhedron of **2<sup>II</sup>** is distorted to provide more trigonal pyramidal geometry (the  $\Delta\mathcal{Z}(\angle\text{C–Cu–C})$  is increased by ca. 7–10 $^{\circ}$ ). The contact Cu…I (3.9988(6)  $\text{\AA}$ ) was found in **2<sup>II</sup>** and a similar contact was not identified in **2<sup>I</sup>**.

#### S2.4. Molecular structure of $\mathbf{2}\cdot\frac{1}{2}\text{I}_2$ .

**Table S3.** Short contacts in the structure of  $\mathbf{2}\cdot\frac{1}{2}\text{I}_2$ .

Contact	Distances, $\text{\AA}$	Angles, $^{\circ}$	Comments
I4…I1	I4…I1 3.3658(6)	I4–I4…I1 174.23(2) I4…I1–I2 148.130(15)	HaB
I3…I3	I3…I3 3.5172(8)	I2–I3…I3 157.181(19)	Type I contact
I2…C19	I2…C19 3.600(5)	I1–I2…C19 91.21(6)	
I2…Cu1	I2…Cu1 3.9387(6)		

**S2.5. The XRD structure of 3.** The crystal structure of this ionic complex consists of the cation  $[\text{Cu}(\text{CNXyl})_3]^+$  and the pentaiodide anion,  $\text{I}_5^-$ . The bond angles around the copper(I) center are in the range 115.7(3)–128.2(3) $^\circ$ ; the complex exhibits a trigonal planar geometry. Only two examples of 3-coordinated homoleptic copper(I) isocyanide species have been previously reported and they include the  $[\text{Cu}_2\{\mu-1,1'-(\text{CN})_2\text{Fc}\}_3][\text{PF}_6]_2\cdot\text{CHCl}_3$ <sup>14</sup> and  $[\text{Cu}(\text{CNCH}_2\text{CMe}_2\text{OMe})_3][\text{BF}_4]$ <sup>15</sup> complexes, where both copper(I) centers exhibit a trigonal planar geometry.

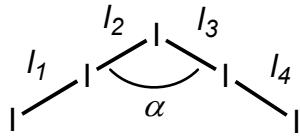
In **3**, the pentaiodide anion exhibit a V-shaped geometry that is typical for  $\text{I}_5^-$ .<sup>16-18</sup> The terminal I–I bonds in  $\text{I}_5^-$  are 2.7903(6) and 2.7817(8) Å, the internal I–I bonds are 3.0835(6) and 3.1107(8) Å, and the angle (108.94(2) $^\circ$ ) at the central I atom is usual for pentaiodides.<sup>19</sup> The Cu center and the central I atom of the  $\text{I}_5^-$  anion form the Cu…I short contacts (3.42515(11) Å) that are responsible for the 1D-assembly (**Figure 6**). These distances are well comparable with those in some copper(II) triiodide complexes such as, for example,  $[\text{Cu}\{(\text{C}_2\text{H}_4\text{N}_2\text{Bu})(\text{C}_2\text{H}_4\text{N}_2\text{S}^n\text{Bu}\}\}_2](\text{I}_3)_2$  (DACPQIK: 3.3579(3) Å) or  $[\text{Cu}(\text{Py})_4](\text{I}_3)_2$  (ISAFIS01: 3.3928(2) Å); and also copper(I) trinuclear complex  $[\text{Cu}_3(2,7\text{-bis}(\text{tetramethylguanidino})\text{-1,8-naphthyridine})_2](\text{I}_5)_2(\text{I}_3)$ , bearing semicoordinated  $\text{I}_5^-$  (EWUCOQ002 ( $R_w$  = 5.48%): 3.3977(9) and 3.9217(10) Å).<sup>20</sup> The cations  $[\text{Cu}(\text{CNXyl})_3]^+$ , where aryl rings lie in one plane, interact with each other via the stacking of the aryl rings and C(sp<sup>3</sup>)–H…arene contacts.

This contact can be attributed as a semicoordination bond, which is rather conventional for copper(II) centers because of the Jahn–Teller distortion,<sup>21</sup> but copper(I) centers are quite rarely involved in the semicoordination.

Ongoing from **2·½I<sub>2</sub>** to **3**, the  $d(\text{Cu–I})$  bond length is drastically lengthened (by 0.49 Å) that result in the cationic planar ( $\Delta\Sigma(\angle\text{C–Cu–C})$  360 $^\circ$ ) complex  $[\text{Cu}(\text{CNXyl})_3]^+$ , which forms two equivalent Cu…I semicoordination bonds (3.42515(11) Å) with two  $\text{I}_5^-$  anions.

### S3. CSD search results

#### S3.1. Results of the CSD search for $I_5^-$ anion



**Table S4.** Results of CSD search for  $I_5^-$  anion.

CCDC code	I1–I2, Å	I2–I3, Å	I3–I4, Å	I4–I5, Å	$\angle I_2-I_3-I_4, {}^\circ$
ABUYOO	2.813	3.034	2.976	2.848	93.1
AGODUY	2.797	3.107	3.019	2.840	90.8
AHEWIT	2.872	2.988	3.378	2.756	81.5
AHEWOZ	2.939	2.904	3.396	2.755	85.5
AYAVUS	2.840	2.994	3.272	2.720	114.2
AZIBUH	2.810	3.112	3.008	2.856	94.09
AZICUI	2.816	3.063	3.093	2.793	106.1
BABPON	2.833	3.045	3.172	2.767	81.4
BICGUQ	2.838	3.033	3.033	2.797	89.5
BICHAX	2.828	3.029	3.103	2.785	91.6
BIWMOK	2.822	3.054	3.054	2.822	111.0
BUTNIP	2.829	3.016	3.163	2.775	82.7
CUTXAT	2.798	3.085	3.181	2.791	97.3
DIQYAG	2.790	3.123	3.279	2.768	97.2
DOVQOU	2.782	3.144	3.144	2.782	86.3
DULZOZ03	2.794	3.140	3.140	2.794	95.0
EGOZAB	2.790	3.115	3.187	2.774	99.2
EHASIS	2.806	3.113	3.113	2.806	123.6
ETCBFE	2.799	3.148	3.015	2.837	88.2
EWEKUP	2.885	2.943	3.221	2.746	87.2
EWELAW	2.798	3.152	3.082	2.814	91.0
EWELOK	2.906	2.902	3.241	2.770	87.4
FEKKAJ	2.814	3.067	3.128	2.767	86.8
FIKLAS	2.870	2.974	3.262	2.740	89.8
GEPYOOQ	2.834	3.052	3.143	2.794	112.6
GOBFUY	2.783	3.140	3.140	2.784	87.5
HAWWEK	2.814	3.080	3.080	2.814	86.2
HILLET	2.778	3.154	3.082	2.803	93.6
HIRCAM	2.833	2.974	3.215	2.754	115.2
JARNOI	2.822	3.021	3.073	2.788	95.8
JARNOI	2.836	3.010	3.109	2.765	86.3
JIWGOL	2.800	3.221	3.221	2.800	172.8
JUPDEF	2.842	3.025	3.219	2.776	96.2
KAXZUH	2.828	3.004	3.033	2.817	97.1
KESTIO	2.797	3.056	3.012	2.815	97.9
KEXYAO	2.815	3.064	3.139	2.780	92.5
KEXYIW	2.782	3.137	3.162	2.788	78.5
KEXYIW	2.826	3.072	3.234	2.765	90.6
KIFSOJ	2.845	2.997	3.196	2.769	82.5

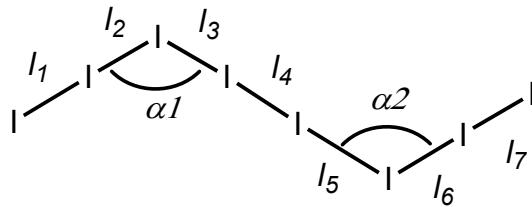
LEBPEP	2.839	3.037	3.229	2.768	95.9
LIVVUK	2.806	3.072	3.222	2.770	88.8
MECPFF	2.817	3.050	3.178	2.790	90.3
NALGOW	2.829	3.060	3.117	2.793	98.4
NALGOW	2.776	3.153	3.096	2.804	99.6
NOYTAW	2.800	3.067	3.067	2.801	102.0
NUTSUR	2.796	3.080	3.064	2.809	98.5
OCIRAT	2.817	3.079	3.269	2.736	86.0
OHORUY	2.818	3.054	3.160	2.799	96.9
OHUVAR	2.810	3.062	3.190	2.773	91.6
OHUVAR01	2.804	3.170	3.170	2.804	90.1
OLECAK	2.789	3.122	3.059	2.817	87.7
OLIFIB	2.832	3.084	3.084	2.832	96.3
OLIZIS	2.792	3.116	3.116	2.792	102.8
OVUDOZ	2.762	3.150	3.107	2.779	101.3
OVUDOZ	2.776	3.112	3.146	2.764	101.8
PADJEL	2.807	3.134	3.146	2.813	81.4
PANVEH	2.803	3.121	3.040	2.840	90.4
PANVEH	2.800	3.150	3.097	2.804	93.3
PANWIM	2.895	2.981	3.319	2.785	87.1
PANWIM	2.860	2.981	3.366	2.744	86.7
PANXIN	2.779	3.111	3.121	2.783	86.4
PANXIN	2.863	2.975	3.179	2.797	136.3
PEZWID	2.788	3.073	3.230	2.771	81.6
QOVFAI	2.821	3.096	3.235	2.770	86.5
QOVFAI	2.843	3.038	3.394	2.764	112.5
RASHUQ	2.795	3.119	3.143	2.808	95.9
RASHUQ	2.798	3.118	3.101	2.777	90.2
RECKEP	2.802	3.001	3.263	2.743	85.0
RIJFIB	2.804	3.146	3.291	2.748	78.4
RIJFIB	2.822	3.067	3.268	2.754	95.5
RIJFIB	2.793	3.136	3.196	2.766	96.4
SOCSIO01	2.832	2.992	2.992	2.832	89.5
SOCVUD	2.845	2.980	3.178	2.766	92.5
SUTVAE	2.790	3.112	3.112	2.790	84.6
UHAPEY	2.861	3.006	3.287	2.767	98.5
UHAPEY	2.819	3.090	3.217	2.760	83.8
VEXVIE	2.818	3.075	3.063	2.806	89.3
WAJZAK	2.813	3.081	3.008	2.832	113.5
WAYTAR	2.894	2.942	3.291	2.764	102.2
WEDHAQ	2.864	2.968	3.231	2.761	94.4
WERBUQ	2.819	3.052	3.127	2.782	94.5
WERBUQ	2.798	3.050	3.051	2.799	104.3
WURGUM	2.803	3.062	3.230	2.743	97.9
WURHEX	2.831	3.017	3.164	2.754	98.1
WURHEX01	2.840	3.007	3.150	2.766	98.6
XACYUW	2.785	3.101	3.215	2.733	126.3
XAYQIA	2.784	3.066	3.104	2.789	81.1
XIPLIT	2.841	3.015	3.196	2.763	109.9
XIQPUI	2.972	3.023	3.274	2.790	88.4

XIVBEJ	2.811	3.119	3.245	2.742	100.9
YAKWIU	2.934	2.934	3.244	2.748	130.1
ZAGXEK	2.790	3.136	3.198	2.799	91.9
ZEPBIF*	2.794	3.106	3.311	2.768	93.8
ZEZFEP	2.803	3.079	3.084	2.789	84.2
ZIQZUW	2.794	3.086	2.959	2.896	96.6
ZIVXIL	2.812	3.069	3.190	2.781	88.6

The angle  $\alpha$  varies from 78.4 to 172.8°, mean 96.7 and median 93.3°. Terminal bond lengths  $l_1$  и  $l_4$  vary from 2.72 to 2.97 Å, mean 2.80 and median 2.80 Å. Internal bond lengths  $l_2$  и  $l_3$  vary from 2.90 to 3.40 Å, mean 3.11 and median 3.11 Å.

### S3.2. Results of the CSD search for the dianions $I_8^{2-}$

CSD search for dianions  $I_8^{2-}$  gave 17 results ( $R_w < 0.05$ ), 13 structures were found and analyzed:



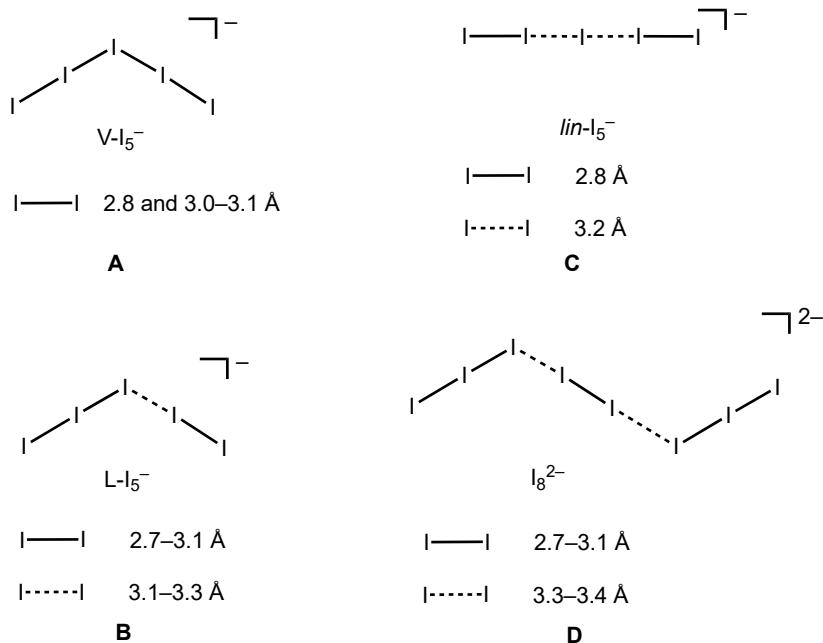
**Table S5.** Results of CSD search anion  $I_8^{2-}$ .

CCDC code	$l_1, \text{\AA}$	$l_2, \text{\AA}$	$l_3, \text{\AA}$	$l_4, \text{\AA}$	$l_5, \text{\AA}$	$l_6, \text{\AA}$	$l_7, \text{\AA}$	$\alpha 1, {}^\circ$	$\alpha 2, {}^\circ$
AZADIP01	2.830	3.044	3.392	2.773	3.392	3.044	2.830	131.4	131.4
CAZCUE	2.813	3.048	3.290	2.776	3.290	3.048	2.813	83.8	83.8
DIWQUV	2.892	2.953	3.362	2.768	3.362	2.953	2.892	85.2	85.2
GIXWIT	2.889	2.979	3.423	2.766	3.423	2.979	2.889	87.8	87.8
GIXWIT	2.876	3.022	3.410	2.791	3.410	3.022	2.876	87.4	87.4
HILLOD	2.829	3.105	3.356	2.780	3.356	3.105	2.829	83.1	83.1
JOPLEH	2.858	3.007	3.442	2.744	3.442	3.007	2.858	160.0	160.0
PONPAJ	2.821	3.022	3.314	2.767	3.314	3.022	2.821	90.4	90.4
VAGKOE	2.796	3.123	3.328	2.788	3.328	3.123	2.796	82.9	82.9
WITLIU	2.866	3.013	3.468	2.754	3.468	3.013	2.866	79.6	79.6
XAGKAT	2.880	2.990	3.378	2.774	3.378	2.990	2.880	99.5	99.5
XENQIK	2.816	3.030	3.267	2.770	3.267	3.001	2.845	89.4	89.6
YUPKEA	2.845	3.017	3.394	2.773	3.394	3.017	2.845	112.1	112.1
ZEZDIR	2.835	3.010	3.394	2.771	3.394	3.010	2.835	98.9	98.9

Analysis of these data indicated that  $l_1$ ,  $l_2$ ,  $l_4$ ,  $l_6$ , and  $l_7$  interatomic distances are belong to covalent I-I bonds. The  $l_3$  and  $l_5$  separations which are in a range 3.27–3.47 Å lie in the “no man’s land” region and they are closer to noncovalent contact values.

### S3.3. CSD search: results and discussion

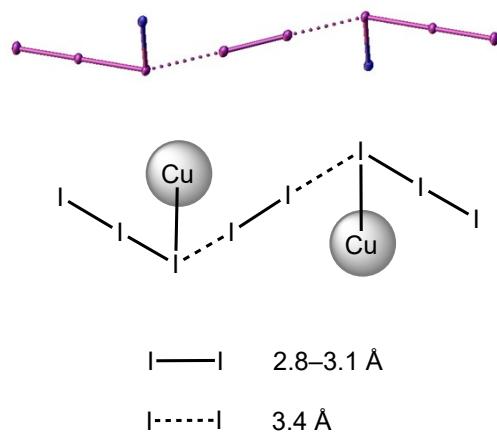
**The known  $I_5^-$  and  $I_8^{2-}$  systems from the CSD search.** Pentaiodide species are usually divided into three categories (**Figure 2**), namely those displaying V- (**A**), L-shaped (**B**), and linear (**C**) geometries.<sup>22</sup> The symmetric V-shaped  $I_5^-$  can be considered as the one built by two  $I_2$  molecules covalently bound to an apical iodide, while the L-shaped pentaiodide is derived from  $I_2$  covalently bound to a triiodide ion. The V-shaped is more symmetrical, while the L-shaped  $I_5^-$  demonstrates the bond length asymmetry. The least abundant linear pentaiodide ion has an  $[(I^-) \cdot 2I_2]$  configuration. Commonly, pentaiodides are linked to each other by intermolecular interactions between terminal atoms or terminal and internal iodine atoms thus forming a variety of structures, spanning from chains to 3D networks.<sup>22</sup> However, the discrete V and L-shaped pentaiodides have also been reported.<sup>22</sup>



**Figure S3.** Relationship between  $\{I_3^- \cdot I_2 \cdot I_3^-\}$  and  $I_5^-$  moieties in **2**·½I<sub>2</sub> and **3**, and bond length-based interpretation of their supramolecular structures.

Our analysis of structural parameters of  $I_5^-$  from CSD (for details see the Supporting Information) indicate that pentaiodide demonstrate difference in covalent distances for the

terminal (2.7–3.0 Å) and internal (3.0–3.4 Å) I–I bonds (**Figure 2A–C**). The overwhelming majority of the analyzed structures includes bent pentaiodides with the central  $\angle(I-I-I)$  lower than 136°. For the symmetric  $V\text{-}I_5^-$ , ca. terminal (2.8 Å) and internal (3.0–3.1 Å) covalent bond lengths are characteristic. In contrast, the L-shaped  $I_5^-$  demonstrates a greater difference in variation of bond lengths: a more symmetric  $I_3^-$  fragment exhibit approx. 2.8 Å of terminal and 2.9–3.1 Å of internal bond lengths, while in the less symmetric fragment  $I\cdots I_2$  distances are 2.7–2.8 Å for terminal and 3.1–3.3 Å for internal bond lengths. A clear boundary between the two forms, V- and L-shaped, was not observed leading to a continuum of intermediate states. At the same time, the extreme cases of L-shaped  $I_5^-$  can be considered as the supramolecular adducts  $\{I_3^-\cdot I_2\}$ .

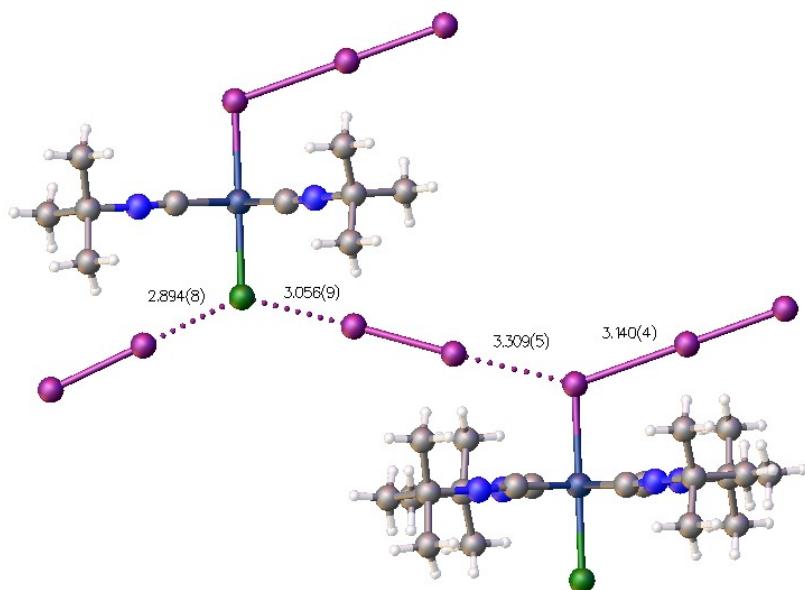


**Figure S4.** View of  $I_3^-\cdot I_2\cdot I_3^-$  associate in the structure of  $2\cdot \frac{1}{2}I_2$ : a fragment of the XRD structure (top panel) and schematic representation with interatomic distances (bottom panel).

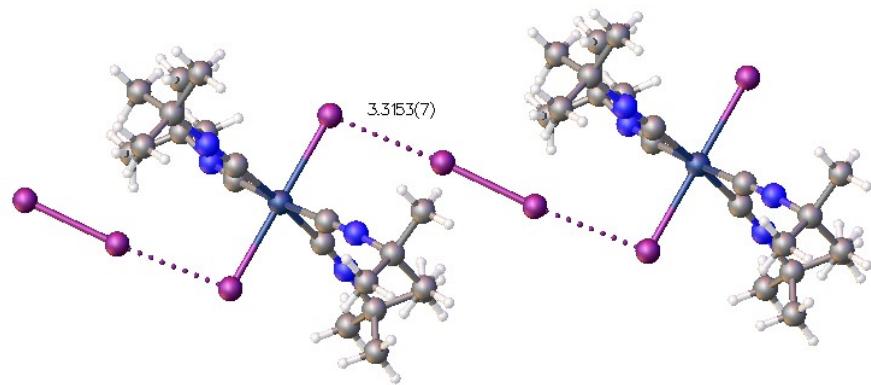
We also analyzed available CSD data for the structures, bearing  $I_8^{2-}$  moiety (**Figure S3**); this dianion is highly relevant to the supramolecular pattern  $\{I_3^-\cdot I_2\cdot I_3^-\}$  observed in the structure of  $2\cdot \frac{1}{2}I_2$  (**Figure 3**). As it follows from the bond length analysis (**Table S5**), all  $I_8^{2-}$  structures can be interpreted as the associates  $\{I_3^-\cdot I_2\cdot I_3^-\}$ , where interatomic distances within the structural units ( $I_2$ ,  $I_3^-$ ) belong to covalent bonds (2.74–3.12 Å) and the shortest separations between these units

are in the 3.27–3.44 Å range, i.e. lie in the “no man’s land” region (3.1–3.4 Å) of the ambiguous attribution next to noncovalent contacts area.

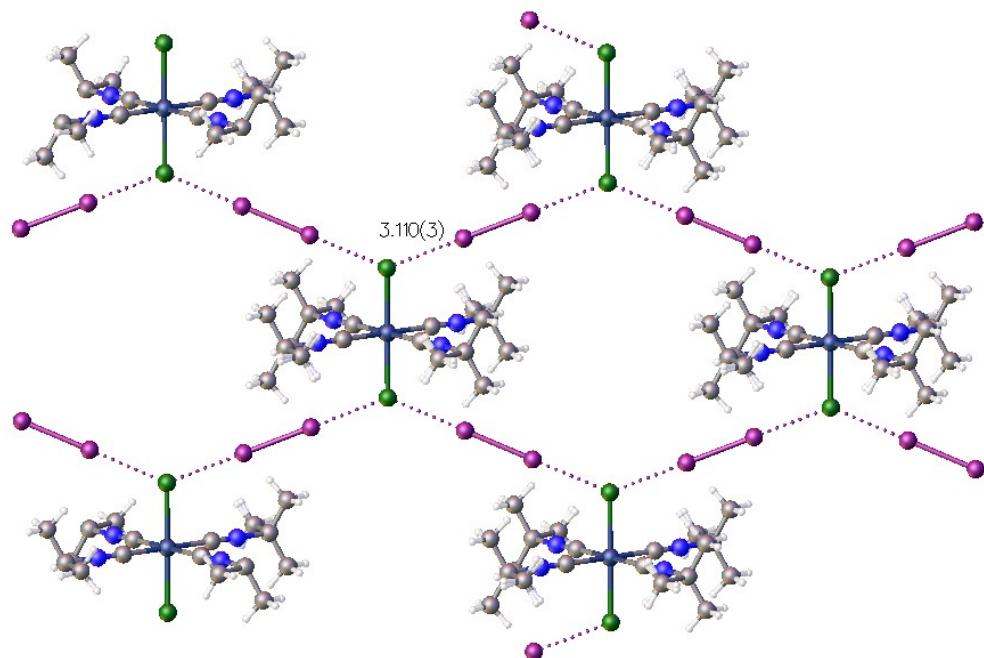
**CSD search for  $\{I_3^-\}_m \cdot \{I_2\}_n$  adducts and related systems bearing coordinated  $I_3^-$ .**  $[Ru(I_3)(ClI_2)(CNBu-t)_4] \cdot I_2$  (ZAGTEJ;  $R_w = 13.02$ ),<sup>23</sup> bearing both  $I_3^-$  and  $ClI_2^-$  ligands, contains  $\{I_3^- \cdot I_2 \cdot ClI_2^-\}$  moieties featuring rather strong  $I \cdots Cl$  (3.056(9) Å; Nc 0.82) and  $I \cdots I$  (3.309(5) Å; Nc 0.84) noncovalent interactions (**Figure S5**). The supramolecular organization, as reported,<sup>23</sup> is based on end-on-coordinated  $I_3^-$  and  $ClI_2^-$  trihalides, interconnected by  $I_2$  thus forming a 1D solid-state system. Interestingly, that this structure represents an intermediate of the reaction between  $[RuCl_2(CNBu-t)_4]$  and  $I_2$  leading to  $[RuCl_2(CNBu-t)_4] \cdot I_2$  (ZAGTAF; **Figure S6**). Authors<sup>23</sup> consider the structure of  $[RuCl_2(CNBu-t)_4] \cdot I_2$  either as constructed from  $\{I^- \cdot I_2 \cdot I^-\}$  blocks ( $I \cdots I$  separations are 3.3153(7) Å, Nc 0.84) or bearing metal-bound  $I_4^{2-}$ . Such binding, together with coordination of  $I^-$  to the metal center, leads to the formation of 1D chains. Another isolated intermediate of this reaction system is  $[RuCl_2(CNBu-t)_4] \cdot 2I_2$  (ZAGSUY,  $R_w$  6.45; **Figure S7**), whose structure contains HaB-based infinite chains  $\{Cl^- \cdot 2I_2\}_n$  (Cl–I distance 3.110(3) Å, Nc 0.83). Together with coordination of  $Cl^-$  to  $Ru^{II}$  these result in honeycomb organization of structure.



**Figure S5.** View of  $I \cdots I/Cl$  short contact-based supramolecular organization of structure ZAGTEJ bearing metal-bound  $I_3^-$ .



**Figure S6.** View of  $\text{I}\cdots\text{I}$  short contact-based supramolecular organization of structure ZAGTAF.

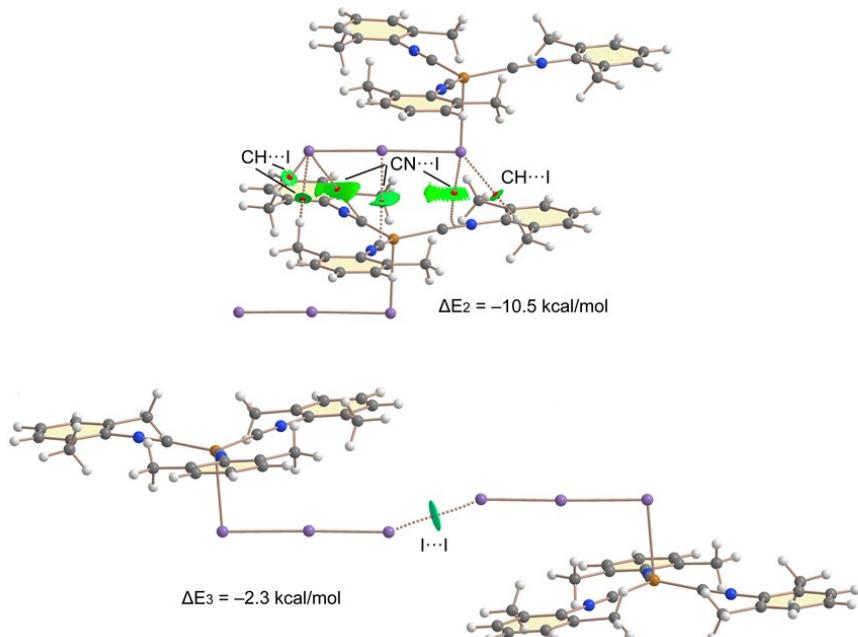


**Figure S7.** View of  $\text{I}\cdots\text{I}$  short contact-based supramolecular organization of structure ZAGSUY.

Lead polyiodide complex can also be considered as a relevant example, both to coordinated and free polyiodides. Its structure featuring  $(2\text{I}_3\cdot\text{I}_2)^{2-}\text{n}$ -based polymeric chain<sup>24</sup> and the metal centers form weak  $\text{Pb}\cdots\text{I}$  contacts with this chain.

## S4. Computational studies

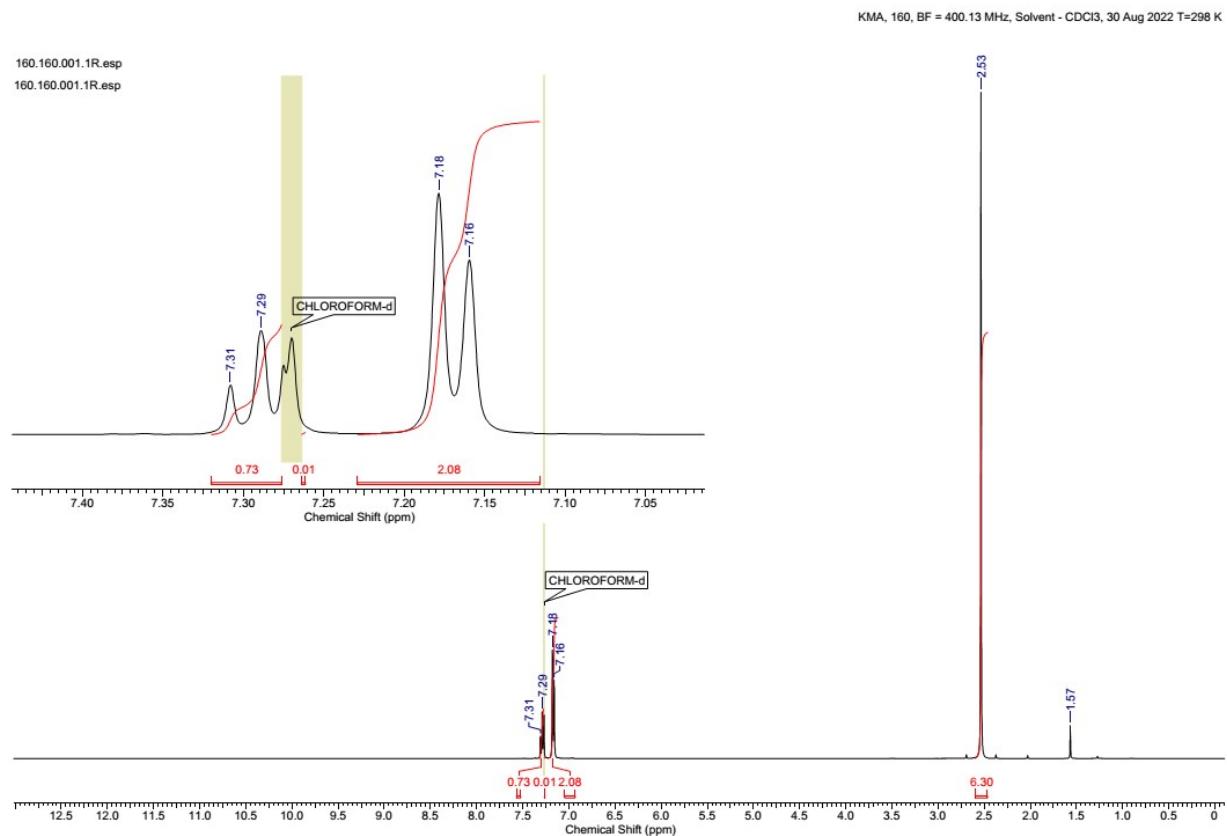
The  $(\mathbf{2})_2$  dimers with other interactions are given in **Figure S8**, where the  $\text{I}_3^-$  ligand interacts with the  $\text{Cu}(\text{CN})_3$  core (top panel) or with the  $\text{I}_3^- \cdots \text{I}_3^-$  contact (bottom panel). In the former case, the QTAIM and NCIplot reveal the existence of three  $\text{CH} \cdots \text{I}$  contacts and another three  $\text{I} \cdots (\text{CN})$  that are characterized by the corresponding bond CPs, bond paths and green isosurfaces. The dimerization energy is moderately strong ( $\Delta E_2 = -10.5 \text{ kcal/mol}$ ) due to the intricate combination of interactions.



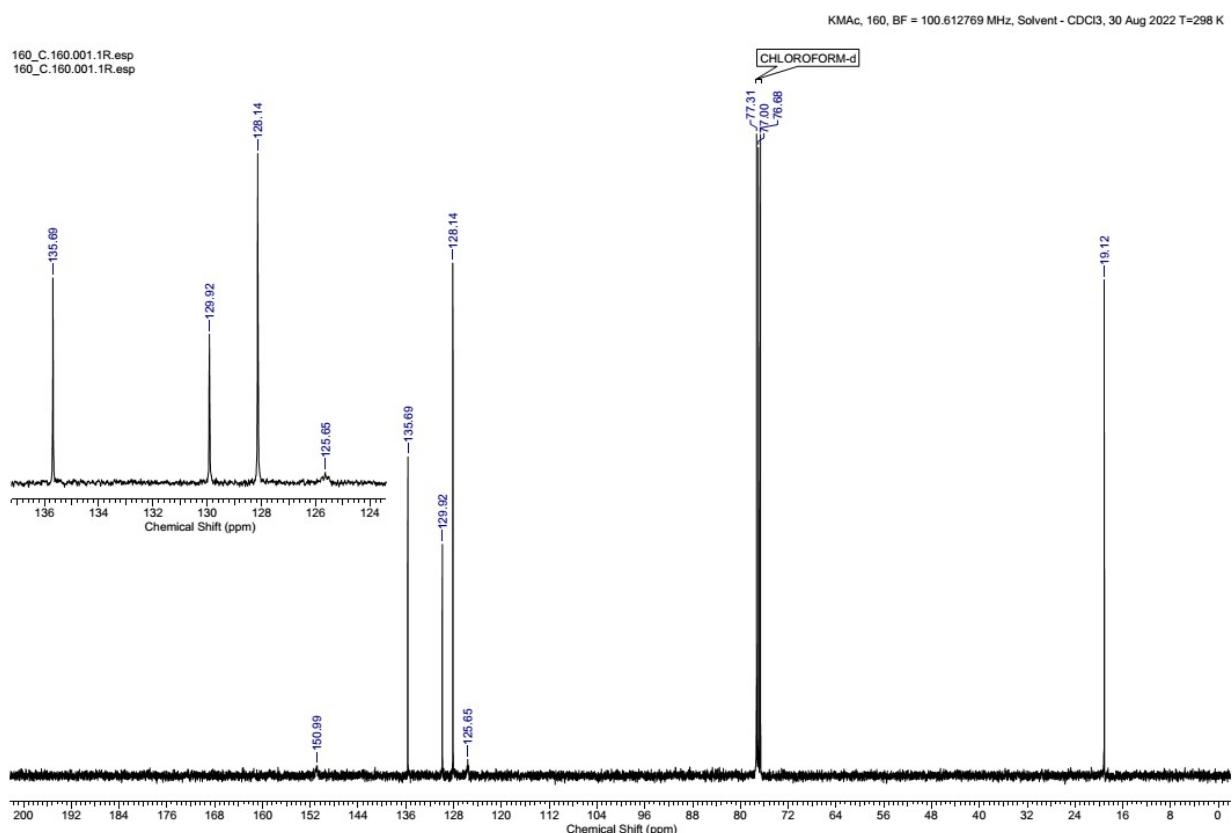
**Figure S8.** QTAIM/NCIPlot analyses in  $(\mathbf{2})_2$  dimers with  $\text{CH} \cdots \text{I}$  and  $\text{I} \cdots (\text{CN})$  interactions (top panel) and the  $\text{I}_3^- \cdots \text{I}_3^-$  Type-I halogen-halogen interaction (bottom panel). The dimerization energies computed at the PBE-D3/def2-TZVP are indicated. Only intermolecular contacts are represented by bond CPs and RDG isosurfaces.

In the latter case, the  $\text{I}_3^- \cdots \text{I}_3^-$  contact (Type-I halogen-halogen interaction; **Figure S8**), was confirmed by a bond CP and bond path connecting the I-atoms. Moreover, the green RDG isosurface located coincident to the bond CP confirms the attractive nature of the interaction. This fact is also supported by the computed dimerization energy, which is small and attractive ( $\Delta E_3 = -2.3 \text{ kcal/mol}$ ).

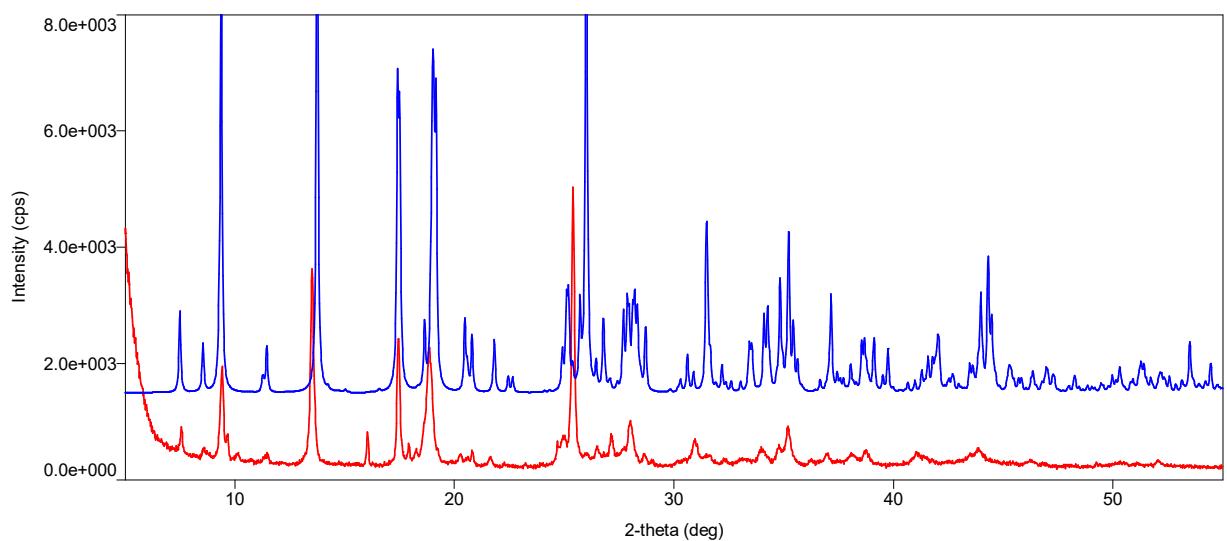
## S5. NMR spectra and powder X-ray diffraction data



**Figure S9.** <sup>1</sup>H NMR spectrum of [CuI<sub>5</sub>(CNXyl)<sub>3</sub>] (3) (CDCl<sub>3</sub>, 400 MHz).



**Figure S10.** <sup>13</sup>C NMR spectrum of [CuI<sub>5</sub>(CNXyl)<sub>3</sub>] (3) (CDCl<sub>3</sub>, 100 MHz).



**Figure S11.** The measured powder X-ray diffraction pattern of **3** (red) and simulated X-ray diffraction patterns of **3** (blue).

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