Guanidine Electron Donors and Silver Halides: Interplay and Competition between Redox, Coordination and Polymerization Reactions

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Redox reactions compete with coordination and polymerization reactions when the organic electron donor and ligand, 1,2,4,5-tetrakis(tetramethylguanidino)benzene (1), is dissolved together with silver halides AgX (X = Cl, Br or I) in solvents of different polarity. The complex results obtained

Introduction

Aromatic compounds with amino substituents in a para position to each other are well-known organic electron donors. Examples include 1,4-bis(dimethylamino)benzene and 1,2,4,5-tetrakis(dimethylamino)benzene.^[1] Oxidation of 1,4bis(dimethylamino)benzene leads to "Wurster's blue". which was described as early as the end of the 19th century.^[2] Recently, aromatic compounds functionalized by several guanidino groups in a para position to each other (GFA-n, whereby n denotes the number of guanidino substituents) were introduced as a new class of strong organic electron donors.^[3-9] Two examples for GFA-4 compounds are 1,2,4,5-tetrakis(tetramethylguanidino)benzene^[3] (1) and 1,2,4,5-tetrakis(N,N'-dimethyl-N,N'-ethyleneguanidino)benzene^[9] (2) (see Scheme 1). In comparison to the corresponding amines, 1 and 2 are much stronger Brønsted bases and exhibit a higher reduction capacity. For example, the oxidation potential $E_{1/2}(CH_2Cl_2) = 0.063 V$ for 1,2,4,5-tetrakis(dimethylamino)benzene^[10] but -0.32 V for 1^[3] with respect to SCE. In addition, as shown in a massive body of work, guanidines are versatile ligands that have been used extensively for the synthesis of molecular compounds for manifold applications (e.g., catalysis or deposition of materials from precursors).[11–15]

GFA-4 compounds such as 1 could be engaged in different reaction types like redox reactions, Brønsted acidbase reactions and reactions to give coordination compounds. In some cases, they compete with each other, and in others they are coupled. Of course, N ligands generally

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NMe₂ NMe₂ NMe MeN NMe₂ NMe Мe Me NMe NMe₂ MeN NMe NMe₂ NMe₂ 2 1

for the relatively simple system 1/AgX highlight the impor-

tance of solvent effects. A variety of chain polymers have

been synthesized in which the guanidine electron-donor

building blocks are connected by silver halide clusters of dif-

Scheme 1.

ferent sizes.

represent Brønsted bases, and in fact protonation can be considered the simplest model for complex formation. However, compounds such as 1 or 2 represent superior organic Brønsted bases, much stronger than amines, for example, and therefore readily deprotonate weak proton acids and solvents such as CH₃CN if supporting conditions {e.g., the presence of [Au(PPh₃)Cl]} are fulfilled.^[9] In the past we reported several examples of the chemistry of 1, in which oxidation and coordination are coupled.^[4,5] This is possible because 1 could act as a ligand even after two-electron oxidation, thereby underlining its extremely strong Lewis base character. For example, treatment of a solution of 1 with Cu(BF₄)₂ in CH₃CN yielded a dinuclear complex of the guanidine dication, $[1{Cu(NCCH_3)_4}_2](BF_4)_6$.^[4] In this case, a redox reaction is coupled with coordination. On the other hand, Brønsted acid-base reactions compete with coordination reactions and usually also with redox reactions. One example is provided by the treatment of a solution of 2 with [AuCl(PPh₃)] and PhCCH in CH₃CN.^[16] In this case, the redox channel that leads to the salt 2[Au(CCPh)₂]₂ and the Brønsted acid-base channel that leads to the neutral Au complex [Au(PPh₃)CCPh] exhibit similar kinetics in CH₃CN. Consequently, a roughly equimolar mixture of

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both product types results. Of course, the solvent is of great importance, and highly polar solvents favour the redox channel.

Herein we present examples of the chemistry of 1 in which coordination, redox and polymerization reactions interplay and/or compete with each other. Variations in the experimental conditions, especially the polarity of the solvent, favour one channel over the other. Oxidation of the guanidine is accompanied by an intense green colouring of the solution. The reaction between a silver halide and a guanidine, which at first glance appears to be very simple, will be shown to be a complex story. Chain polymers that contain ordered arrays of silver halide clusters connected through guanidine electron-donor units are among the structurally characterized products.

Results and Discussion

In the following we discuss the reactions of 1 with silver halides in solvents of different polarities. In the reaction equations we took care to ensure that the stoichiometry of the reactants is correct; they generally are not balanced. The yields refer to the isolated crystalline material and are therefore generally lower bounds for the actual yield. Due to the manifold possible reaction pathways, most reaction products cannot be foretold; however, it will be shown that the reactions could be directed in one direction by optimization of the reaction conditions.

Reactions in MeOH

When 1 was treated with AgCl or AgBr at room temp. in MeOH, the solution turned, after a few minutes, a deep green that is characteristic of oxidized 1. The analytical data (see the Experimental Section) show the products to be the salts (1)X₂ [X = Cl or Br, formed according to Equation (1)]. Hence the ¹H NMR spectra of a solution of (1)Br₂ in CD₃CN displays signals of the dication 1²⁺ (methyl groups and aromatic C–H) at δ = 2.88 and 5.16 ppm.

$$1 + 5 \text{ AgX} \xrightarrow{\text{CH}_3\text{OH}} (1)X_2 + \text{Ag}$$

$$X = \text{Cl or Br} \qquad X = \text{Cl: } 70\%$$

$$X = \text{Br: } 68\% \qquad (1)$$

For comparison, the ¹H NMR spectroscopic signals of the neutral guanidine 1, also dissolved in CD₃CN, occur at $\delta = 2.63$ and 5.54 ppm, and that of the dication in 1(I₃)₂ at $\delta = 2.88$ and 5.17 ppm.^[3] The UV/Vis spectrum of (1)Br₂ dissolved in CH₃CN (see Figure 1) contains three strong absorptions centered at $\lambda = 218$, 293 and 416 nm. In addition, a weak and broad feature occurs at 589 (614) nm (see inset in Figure 1). Single crystals of (1)Cl₂ and (1)Br₂·4MeOH suitable for XRD were obtained from CH₃CN/Et₂O and MeOH/Et₂O solutions, respectively. Figure 2 illustrates the structures. As known from other salts,



Figure 1. UV/Vis spectrum of (1)Br₂ dissolved in CH₃CN.



Figure 2. Structures of the salts (1)Cl₂ and (1)Br₂. Thermal ellipsoids drawn at the 50% probability level. Selected structural parameters {(bond lengths [pm], bond angles [°]) for (1)Cl₂: N1-C1 129.9(2), N1-C7 137.0(2), N2-C7 133.4(3), N3-C7 134.0(3), N4-C2 133.8(2), N4-C12 134.8(2), N5-C12 133.9(2), N6-C12 134.9(2), N7-C4 130.3(2), N7-C17 136.4(2), N8-C17 135.0(2), N9-C17 132.9(2), N10-C5 134.7(2), N10-C22 134.6(2), N11-C22 135.1(2), N12-C22 134.2(2), C1-C2 150.2(2), C1-C6 141.6(2), C2-C3 137.6(2), C3-C4 142.2(2), C4-C5 150.6(2), C5-C6 137.2(2); C1-C2-N4-C12 N1-C7 129.44(15), 122.79(14), C4-N7-C17 125.48(15), C5-N10-C22 122.59(14), N2-C7-N3 121.09(17), N5-C12-N6 118.74(16), N8-C17-N9 121.17(15), N11-C22-N12 118.68(15). Selected structural parameters (bond lengths [pm], bond angles [°]) for (1)Br₂: N1-C1 135.17(19), N1-C4 133.97(19), N2-C4 135.26(19), N3-C4 134.75(19), N4-C2 130.64(19), N4-C9 136.94(19), N5-C9 134.30(19), N6-C9 132.65(19), C1-C2 149.9(2), C1-C3 137.3(2), C2-C3' 141.8(2); C1-N1-C4 122.58(13), N2-C4-N3 117.96(13), C2-N4-C9 125.54(13), N5-C9-N6 121.13(13).

the guanidine dication can be described as a pair of bisguanidino-allyl monocations that are connected by two C-C single bonds [distances of 150.2(2) and 150.6(2) pm for C1-C2 and C4-C5 in (1)Cl₂, and of 149.9(2) pm for C1-C2 in (1)Br₂]. Treatment of 1 with AgI yielded a product mixture from which we isolated in a crystalline yield of 51% a brown-red chain polymer of the formula $[1(Ag_6I_8)]_n$; see Equation (2). The polymer is insoluble in CH_3CN , but to some degree soluble in DMF. Crystals of this polymer were obtained with and without cocrystallized DMF solvate molecules. Fractions of the obtained structures are visualized in Figure 3. It can be seen directly that the structures are significantly different. In the case of $[1(Ag_6I_8)\cdot 2DMF]_n$, the chain can formally be regarded to consist of $[1(AgI_2)_2]$ units fused together by neutral chair-type-structured Ag₄I₄ clusters. The organic building blocks are directly incorporated into the main chain of the polymer. In the case of solvatefree crystals of $[1(Ag_6I_8)]_n$, chains of rhombic Ag_2I_2 units connected through the corners can be identified. Every second rhombic unit is bound through the Ag atoms to two $[1(AgI_2)_2]$ units. Hence in this case the organic building blocks are not incorporated into the polymer main chain.



Figure 3. Fractions of the crystal structures of the coordination polymers (a) $[(1)Ag_6I_8:2DMF]_n$ and (b) $[(1)Ag_6I_8]_n$ (hydrogen atoms omitted). Thermal ellipsoids drawn at the 50% probability level.

Reactions in CH₃CN

Reactions in CH₃CN proceeded very differently. Hence in the case of AgBr and AgI, no oxidation of guanidine 1 was observed. Instead, the guanidine acted as a chelating ligand and pale yellow coordination polymers $[1(AgX)_2]_n$ (X = Br or I) were formed; see Equation (3). Crystals of the chain polymer [1(AgBr)₂]_n suitable for single-crystal X-ray diffraction (XRD) were grown from concentrated CH₃CN solutions. The structure is illustrated in Figure 4. Each Ag^I is tetrahedrally coordinated by two N and two Br atoms. The dihedral angle between the N-Ag-N and Br-Ag-Br planes is close to the ideal value of 90° for tetrahedral coordination. All polymer chains run into the same direction (see Figure 4). The Ag-N bond lengths measure 236.0(2) and 233.8(2) pm. With 72.6(1)°, the N-Ag-N bond angles are relatively small. The Br-Ag-Br angles [100.3(3)°] are close to the ideal value for tetrahedral coordination. The polymer $[1(AgI)_2]_n$ was obtained in a similar way by reaction between 1 and two equivalents of AgI in CH₃CN solutions. Crystals of $[1(AgI)_2 \cdot 4DMF]_n$ were obtained after sev-



Figure 4. A part of the structure of the coordination polymer $[1(AgBr)_2]_n$ (hydrogen atoms omitted). The alignment of the onedimensional polymers is shown below. Thermal ellipsoids drawn at the 50% probability level. Selected structural parameters (bond lengths [pm], bond angles [°]): Ag–Br1 273.23(7), Ag–Br1' 268.47(8), Ag–N1 236.0(2), Ag–N4 233.8(2), N1–C1 140.9(3), N1– C4 130.9(3), N2–C4 138.3(3), N3–C4 136.5(3), N4–C2 141.0(3), N4–C9 131.5(3), N5–C9 138.0(3), N6–C9 135.4(3), C1–C2 140.7(3), C1–C3 139.3(3), C2–C3' 140.0(3); N1–Ag–N4 72.63(7), Br1–Ag–Br1' 100.25(3).

eral weeks from concentrated DMF solutions. The structure is visualized in Figure 5. The polymer chains are structurally similar to those in $[1(AgBr)_2]_n$. The cocrystallized DMF molecules separate two adjacent polymer chains. Unlike $[1(AgBr)_2]_n$, every second chain in $[1(AgI)_2 \cdot 4DMF]_n$ is tilted by approximately 90° around the chain axis (see Figure 5).

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Figure 5. A part of the structure of the coordination polymer $[1(AgI)_2]_n$ (hydrogen atoms omitted). The alignment of the onedimensional polymers is shown below. Thermal ellipsoids drawn at the 50% probability level. Selected structural parameters (bond lengths [pm], bond angles [°]): Ag–I1 276.49(7), Ag–I1' 291.83(8), Ag–N1 234.31(18), Ag–N4 237.17(18), N1–C1 141.1(2), N1–C11 131.8(3), N2–C11 136.7(2), N3–C11 136.4(3), N4–C2 141.4(2), N4– C16 130.4(3), N5–C16 137.5(2), N6–C16 137.9(3), C1–C2 140.9(3), C1–C3' 139.6(3), C2–C3 139.3(3); I1–Ag–I1' 110.74(3), N1–Ag– N4 73.92(6).

For treatment of AgCl with 1, a product mixture was obtained. In a crystalline yield of 23%, compound [1(AgCl)₂] was isolated, which is a dinuclear coordination compound, unlike the polymers of similar overall formula obtained in the reactions with AgBr or AgI. Its structure is illustrated in Figure 6. The molecular units are arranged in stacks. In addition, the salt $(1)Cl_2$ (11% yield) and the chain polymer $[1(Ag_4Cl_6)]_n$ (21% yield) were formed; see Equation (4). The latter was crystallized either from $CHCl_3$ as $[1(Ag_4Cl_6)\cdot 4CHCl_3]_n$ or from CH_2Cl_2 as $[1(Ag_4Cl_6)\cdot$ 2CH₂Cl₂]_n. The structures of the polymers with CHCl₃ and CH_2Cl_2 solvate molecules are compared in Figure 7. The chains found in both compounds could be considered to consist of a cationic polymer $\{[1(AgCl)_2]^{2+}\}_n$ in which the building blocks are connected by halide bridges. The silver and halide atoms of each [1(AgCl)2]2+ unit interact with two [AgCl₂]⁻ anions. However, the conformation of the chains differs significantly. Hence the dihedral angle between the central Ag₂Cl₂ ring plane and the N-Ag-N planes amounts to 72° in [1(Ag₄Cl₆)·4CHCl₃]_n, and 34° in

 $[1(Ag_4Cl_6)\cdot 2CH_2Cl_2]_n$. Both compounds decompose in MeOH solutions. The analytical data indicate formation of AgCl and (1)Cl₂ as decomposition products.



Figure 6. (a) Molecular structure of $[1(AgCl)_2]$ (hydrogen atoms omitted). Thermal ellipsoids drawn at the 50% probability level. Selected structural parameters (bond lengths [pm], bond angles [°]): Ag–Cl 237.12(11), Ag–N1 226.3(2), Ag–N4 232.9(2), N1–Cl 142.4(3), N1–C4 131.6(4), N2–C4 136.4(3), N3–C4 137.0(4), N4–C2 141.4(3), N4–C9 130.9(4), N5–C9 137.3(4), N6–C9 136.1(4), C1–C2 141.6(4), C1–C3' 139.2(4), C2–C3 139.5(4); N1–Ag–N4 75.07(8), Cl–Ag–N1 153.81(6), Cl–Ag–N4 131.01(6).



Figure 7. Parts of the crystal structures of the coordination polymers (a) $[1(Ag_4Cl_6)\cdot 4CHCl_3]_n$ and (b) $[1(Ag_4Cl_6)\cdot 2CH_2Cl_2]_n$ (hydrogen atoms omitted). Thermal ellipsoids drawn at the 50% probability level.

Reactions in Toluene

If the reaction between 1 and AgCl was carried out in toluene, only the coordination compound $[1(AgCl)_2]$ with a neutral guanidine ligand was formed in 77% crystalline yield; see Equation (5). The same compound was already obtained as one of the products of the reaction between 1 and AgCl in CH₃CN. Further experiments with this complex showed it to be stable only in apolar solvents. When it was dissolved under heat in CH₂Cl₂, a redox reaction was initiated to yield the coordination polymer $[1(Ag_4Cl_6)]_n$ – see Equation (6) – which was already shown to be one of the products of reaction between 1 and AgCl in CH₃CN.

1 + 2 AgCl
$$\xrightarrow{C_7H_8}$$
 [1(AgCl)₂]
77% (5)

$$3/n \left[\mathbf{1}(\mathsf{AgCl})_2 \right] \xrightarrow{\mathsf{CH}_2\mathsf{Cl}_2} 1/n \left[\mathbf{1}(\mathsf{Ag}_4\mathsf{Cl}_6) \right]_n + 2 \operatorname{Ag}$$
(6)

Properties of the One-Dimensional Polymers $[1(AgX)_2]_n$ (X = Br or I)

The experiments described above showed that coordination compounds of the neutral guanidines could be obtained by careful choice of the solvent. Whereas [1(AgCl)₂] is a dinuclear compound, $[1(AgBr)_2]_n$ and $[1(AgI)_2]_n$ represent chain polymers. Furthermore, [1(AgCl)₂] is highly amenable to redox reactions when brought into contact with solvents of moderate to strong polarity. In further experiments described in this section, we analyzed the properties and redox chemistry of the polymers $[1(AgBr)_2]_n$ and $[1(AgI)_2]_n$. Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements (see curves in Figure 8) indicate that both compounds are stable up to temperatures of 250 °C. Their remission spectra (see the Supporting Information) contain broad absorptions below 500 nm. When the compounds were heated to a temperature of 650 °C, gas evolution was monitored and the materials changed their optical properties dramatically. The initially yellow colour of the intact polymer turned to black with a metal-like gleam after the heat treatment (see photos provided in the Supporting Information). Up to now we have been unable to characterize the structures of these products of pyrolysis. The elemental analysis showed them to contain substantial amounts of carbon and nitrogen. Further work, which is outside the scope of this article, is necessary to study the composition and properties of these materials.

In our oxidation experiments, $[1(AgBr)_2]_n$ and $[1(AgI)_2]_n$ were treated with I₂ as well as organic electron acceptors [2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachlorobenzoquinone (TCQ) and tetracyanoquinodimethane (TCNQ)]. The results will be briefly summarized in the fol-



Figure 8. TG and DSC curves (at a heating rate of 10 °Cmin⁻¹ under an N₂ atmosphere) for (a) $[1(AgBr)_2]_n$ and (b) $[1(AgI)_2]_n$.

lowing; see Equations (7), (8) and (9). In the case of reaction of an equimolar mixture of $[1(AgBr)_2]_n$ and I_2 at room temp. in CH₃CN, the coordination polymer $[1(Ag_6I_{8-x}Br_x)]_n$ with x = 0.7 was isolated in a crystal yield of 26%. Its structure is depicted in Figure 9 (a). It resembles that of $[1(Ag_6I_8)]_n$. In the case of a 2:1 molar ratio of the two reactants (but otherwise unchanged reaction conditions), a different product was isolated in extremely small but reproducible yield. This product was unambiguously identified as the coordination polymer $[1(Ag_5Br_4I_3)]_n$ (see Figure 9, b). The guanidine building blocks are incorporated into the polymer main chain. The small yield is at

$$\frac{1/n \left[1(AgBr)_{2}\right]_{n} + I_{2}}{r.t.} \quad \frac{CH_{3}CN}{r.t.} \quad \left[1(Ag_{6}I_{8-x}Br_{x})\right]_{n}}{26\%, x = 0.7}$$
(7)

$$\frac{1/n \left[1(\text{Agl})_2 \right]_n + 0.5 I_2}{\text{r.t.}} \quad \frac{\text{CH}_3 \text{CN}}{\text{r.t.}} \quad 1(\text{Agl}_3)$$
11% (9)

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least partially caused by the low solubility of the starting reagents. On the other hand, reaction between $[1(AgI)_2]_n$ and I_2 (0.5 equiv.) yielded not a polymer but the salt 1(AgI₃) with separated guanidine dicationic and AgI₃ dianionic units (see Figure 10).

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Figure 9. Fractions of the crystal structures of the coordination polymers (a) $[1(Ag_6I_{8-x}Br_x)]_n$ with x = 0.7 and (b) $[1(Ag_5Br_4I_3)]_n$.



Figure 10. Structure of the salt 1(AgI₃). Selected bond lengths [pm]: Ag-I1 278.48(6), Ag-I2 275.88(6), N1-C1 134.6(2), N1-C4 134.6(2), N2-C4 135.1(3), N3-C4 135.0(2), N4-C2 130.8(2), N4-C9 136.9(2), N5-C9 134.6(3), N6-C9 133.1(3), C1-C2 150.1(3), C1-C3' 137.5(3), C2-C3 142.2(3).

Treatment of $[1(AgBr)_2]_n$ or $[1(AgBr)_2]_n$ with the organic electron acceptor DDQ (2 equiv.) gave a black product, which was identified as the donor-acceptor couple $1(DDQ)_2$; see Equation (10). The crystal structure is provided in Figure 11. Clearly, this compound can be prepared more directly by reaction between 1 and DDQ. The donor and acceptor units are arranged in stacks. The packing as well as the black appearance of the material make it attractive for a future analysis of the electronic properties. Reaction between $[1(AgI)_2]_n$ and TCQ or TCNQ yielded the polymer $[1(Ag_6I_8)]_n$ - see Equations (11) and (12) - a prod-

uct that also could be obtained more directly by reaction between 1 and AgI in MeOH. This compound seems to be of especial stability, as it is obtained under various conditions.



30%

16%

CH₃CN 1/n [1(Agl)2]n + TCQ $[1(Ag_6I_8)]_n$





(11)



Figure 11. Structure of the salt $1(DDQ)_2$. Selected bond lengths [pm]: cationic guanidine units: N1-C1 130.4(2), N1-C4 137.4(2), N2-C4 134.1(2), N3-C4 133.7(2), N4-C2 135.9(2), N4-C9 133.7(2), N5-C9 135.3(2), N6-C9 135.3(2), C1-C2 150.0(3), C1-C3' 143.2(3), C2-C3 136.6(3); anionic DDQ units: O1-C18 124.4(2), O2-C15 124.7(2), C11-C14 172.3(2), C12-C19 172.5(2), N8-C21 114.3(3), C17-C21 143.3(3), C14-C15 147.6(3), C14-C19 135.3(3), C15-C16 144.4(3), C16-C17 139.1(3), C17-C18 145.0(3), C18-C19 146.6(3).

Conclusion

Coordination, redox and polymerization reactions are either coupled or in competition with each other when the guanidine electron donor 1,2,4,5-tetrakis(tetramethylguanidino)benzene (1) reacts with silver halides in solvents of different polarities. By choice of solvent, the reaction could

be directed into the desired channel. The results of this work are of special importance for the use of guanidine electron donors as building blocks in coordination polymers. In these polymers, the guanidine units are generally highly oxidized and coloured, thus making them attractive for optical and/or electronic applications. This article shows how halide clusters of different sizes could be incorporated into the chain polymers, thereby opening an access route to well-defined arrays of photoactive silver halide clusters. As shown for the pairs of compounds $[1(Ag_6I_8)\cdot 2DMF]_n$ and $[1(Ag_6I_8)]_n$ as well as $[1(Ag_4Cl_6)\cdot 4CHCl_3]_n$ and $[1(Ag_4Cl_6)\cdot 2CH_2Cl_2]_n$, the incorporation of solvent molecules leads to significant changes in the polymer structures.

Experimental Section

General: The synthetic work was carried out under an inert-gas atmosphere by using standard Schlenk techniques. All solvents were dried rigorously prior to their use. UV/Vis spectra were recorded with a Varian Cary 5000 spectrometer. NMR spectra were measured with a Bruker Avance II 400 NMR machine. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. IR spectra were recorded with a Biorad Excalibur FTS3000 spectrometer. Thermogravimetric (TG) and calorimetric (DSC) measurements were carried out with a Mettler TC15 and DSC30 apparatus under a N₂ atmosphere in a temperature range of 30–600 °C. The heating rate was varied between 2 and 10 °C min⁻¹.

Compound (1)Cl₂: AgCl (135 mg, 0.934 mmol) was added to a solution of 1 (100 mg, 0.188 mmol) in CH₃OH (10 mL). The solution was stirred at room temp. for a period of 2 h, during which time the solution quickly adopted a deep green colour. After filtration, 4/5 of the solvent volume was removed, and the initial amount of solvent was restored by the addition of Et₂O. A dark crystalline powder of (1)Cl₂ precipitated; yield 80 mg (0.133 mmol, 70%). Single crystals suitable for XRD were obtained from CH₃CN/Et₂O. $C_{28}H_{58}Cl_2N_{12}O_2$ [M + 2MeOH] (665.75): calcd. C 50.51, H 8.78, N 25.25; found C 49.73, H 8.71, N 25.85. $^1\mathrm{H}$ NMR (400 MHz, CD_2Cl_2): $\delta = 2.76$ (48 H, CH_3), 5.44 (2 H, Ar_H) ppm. ¹³C NMR $(100 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 40.2 \text{ (CH}_3), 111.6, 135.5, 162.7 \text{ ppm. IR}$ (CsI): $\tilde{v} = 2947$, 1608, 1564, 1508, 1467, 1421, 1395, 1304, 1256, 1226, 1187, 1165, 1139, 1057, 1018, 896, 840, 806, 749, 688, 623, 532, 458 cm⁻¹. UV/Vis (CH₃CN, $c = 3.4 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ (ε in $L mol^{-1} cm^{-1}$) = 218 (42148), 293 (16240), 425 (24148) nm. MS-ESI⁺ (MeOH): m/z (%) = 265.3 (100) $[1]^{2+}$, 530.3 (56) $[1]^{+}$, 565.6 (25) $[1 + Cl]^+$. Crystal data for (1)Cl₂, C₂₆H₅₀Cl₂N₁₂: $M_r = 601.68$, $0.30 \times 0.11 \times 0.05$ mm³, orthorhombic, space group *Pca2*(1), *a* = 19.210(4) Å, b = 7.5353(15) Å, c = 21.463(4) Å, V = 3106.8(11) Å³, Z = 4, $d_{\text{calcd.}} = 1.286 \text{ Mg m}^{-3}$, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 1.90$ to 30.58°. Reflections measd. 75068, indep. 9521, $R_{int} = 0.0644$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0430$, $wR_2 = 0.0985$.

Compound (1)Br₂: AgBr (142 mg, 0.755 mmol) was added to a solution of **1** (80 mg, 0.151 mmol) in MeOH (10 mL). The solution was stirred at room temp. for a period of 2 h, during which time the solution quickly turned deep green. Then the solution was filtered and the solvent was partially removed to around 2 mL. A dark, crystalline solid precipitated after the addition of Et₂O (restoring the initial 10 mL volume); yield 71 mg (0.103 mmol, 68%). Crystals suitable for XRD were grown from MeOH/Et₂O. $C_{26}H_{50}Br_2N_{12}$ (690.56): calcd. C 45.22, H 7.30, N 24.34; found C 44.79, H 7.29,



N 23.65. ¹H NMR (400 MHz, CD₃CN): $\delta = 2.88$ (48 H, CH₃), 5.16 (2 H, Ar_H) ppm. ¹³C NMR (100 MHz, CD₃CN): $\delta = 41.48$ (CH₃), 103.90, 157.75, 168.07 ppm. IR (CsI): $\tilde{v} = 2946$, 1608, 1583, 1564, 1505, 1468, 1420, 1390, 1301, 1253, 1227, 1190, 1164, 1142, 1057, 1016, 898, 879, 838, 749, 683, 620, 538 cm⁻¹. UV/Vis (CH₃CN, $c = 6.2 \times 10^{-5} \text{ mol L}^{-1}$): λ (ε in L mol⁻¹ cm⁻¹) = 218 (59431), 293 (16179), 426 (27073), 589 (614) nm. MS-ESI⁺: m/z (%) = 265.3 (100) [1]²⁺, 530.3 (7) [1]⁺, 611.0 (7) [1 + Br]⁺. Crystal data for (1)Br₂·4MeOH: C₃₀H₆₆Br₂N₁₂O₄, $M_r = 818.76$, $0.30 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P2_1/n$, a = 9.4670(19) Å, b = 15.321(3) Å, c = 14.612(3) Å, $\beta = 104.29(3)$, V = 2053.8(7) Å³, Z = 2, $d_{calcd} = 1.324$ Mgm⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 2.33$ to 32.05° . Reflections measd. 14235, indep. 7130, $R_{int} = 0.0366$. Final *R* indices [$I > 2\sigma(I)$]: $R_1 = 0.0374$, $wR_2 = 0.0803$.

Compound [1(Ag₆I₈)]_n: AgI (221 mg, 0.942 mmol) was added to a solution of 1 (100 mg, 0.188 mmol) in MeOH (12 mL). The solution was stirred for a period of 16 h at room temp., during which time the formation of brown-red solid was observed. Then the reaction mixture was filtered and the product dried under vacuum; yield 212 mg (0.097 mmol, 51%). Crystals suitable for XRD were grown from concentrated DMF solutions. Compound [1(Ag₆I₈)]. 2DMF: C₃₂H₆₄Ag₆I₈N₁₄O₂ (2339.39): calcd. C 16.43, H 2.76, N 8.38; found C 16.78, H 2.60, N 8.22. ¹H NMR (400 MHz, $[D_6]DMF$): $\delta = 3.01$ (48 H, CH₃), 5.35 (2 H, Ar_H) ppm. Low solubility hampered the ¹³C NMR spectra. IR (CsI): $\tilde{v} = 2921$, 1677, 1661, 1609, 1577, 1561, 1508, 1492, 1460, 1400, 1384, 1320, 1263, 1231, 1167, 1090, 1022, 897, 813, 785, 737, 701 cm⁻¹. UV/Vis $(CH_3CN, c = 7.9 \times 10^{-6} \text{ mol } L^{-1}): \lambda \ (\varepsilon \text{ in } L \text{ mol}^{-1} \text{ cm}^{-1}) = 245 \ (6827),$ 285 (1827), 426 (2431) nm. MS-FAB⁺: m/z (%) = 531.7 (20) [1 + $H]^+$, 746.5 (1) $[1 + 2Ag]^+$, 784 (2) $[1 + 2I]^+$, 871.0 (7) $[1 + 2I]^+$ $2Ag^{+}I]^{+}$, 891.8 (5) $[1 + Ag + 2I]^{+}$, 978.6 (3) $[1 + 3Ag^{+}I]^{+}$, 1063.3 (1) $[1 + 5Ag - H]^+$. Crystal data for $[1(Ag_6I_8)] \cdot 2DMF$: $C_{16}H_{32}Ag_{3}I_{4}N_{7}O, M_{r} = 1169.70, 0.10 \times 0.10 \times 0.10 \text{ mm}^{3}, \text{ mono-}$ clinic, space group $P2_1/n$, a = 11.727(2) Å, b = 19.456(4) Å, c =12.991(3) Å, $\beta = 94.21(3)^\circ$, V = 2956.0(10) Å³, Z = 4, $d_{\text{calcd.}} =$ 2.628 Mgm⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda =$ 0.71073 Å), T = 100 K, θ_{range} 2.09 to 30.02°. Reflections measd. 16815, indep. 8624, $R_{int} = 0.0600$. Final R indices $[I > 2\sigma(I)]$: $R_1 =$ 0.0442, $wR_2 = 0.0781$. Crystal data for $[1(Ag_6I_8)]$: $C_{13}H_{25}Ag_3I_4N_6$, $M_{\rm r} = 1096.6, 0.15 \times 0.10 \times 0.10 \,{\rm mm^3}$, monoclinic, space group C2/ c, a = 13.795(3) Å, b = 14.615(3) Å, c = 25.803(5) Å, $\beta = 104.82(3)^{\circ}$, $V = 5029.2(19) \text{ Å}^3$, Z = 8, $d_{\text{calcd.}} = 2.897 \text{ Mg m}^{-3}$, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 2.36$ to 28.03°. Reflections measd. 24142, indep. 5969, $R_{int} = 0.0516$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0397$, $wR_2 = 0.0972$.

Compound [1(AgBr)₂]_n: Compound 1 (500 mg, 0.942 mmol) was dissolved in CH₃CN (10 mL). Subsequently, AgBr (354 mg, 1.884 mmol) was added, and the reaction mixture was heated at 90 °C to reflux for a period of 4 h. Then half of the solvent was removed under vacuum from the reaction mixture. The reaction mixture was filtered and washed with a small portion of CH₃CN. The pale yellow product was dried under vacuum to yield 779 mg (0.860 mmol, 91%) [1(AgBr)₂]_n. Crystals suitable for an XRD analysis were obtained from concentrated CH₃CN solutions. C₂₆H₅₀Ag₂Br₂N₁₂ (906.30): calcd. C 34.46, H 5.56, N 18.55; found C 34.31, H 5.56, N 18.36. ¹H NMR (199.92 MHz, CDCl₃): δ = 2.79 (s, 48 H, CH₃), 5.38 (s, 2 H, Ar_H) ppm. ¹³C NMR $(100.55 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 39.94 (CH_3), 110.92, 134.94, 162.10$ ppm. IR (CsI): $\tilde{v} = 2929$ (m), 1515 (s, C=N) , 1382 (s), 1265 (m), 1180 (s), 1063 (m), 1020 (vs), 948 (w), 925 (w), 890 (vs), 867 (s), 776 (m), 712 (m), 573 (m), 426 (w) cm⁻¹. MS-FAB⁺: m/z (%) = 486.1 (34) $[1 - NMe_2]^+$, 531.2 (100) $[1 + H]^+$, 611.2 (2) $[1 + Br]^+$,

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719.3 (0.4) [1 + Ag + Br + H]⁺. UV/Vis (CH₃CN, *c* = 7.37×10⁻⁵ mol L⁻¹): λ_{max} (ε in Lmol⁻¹cm⁻¹) = 218 (5970), 274 (4828), 427 (2460) nm. Crystal data for C₁₃H₂₅AgBrN₆·2CH₃CN: M_r = 535.28, 0.30×0.30×0.27 mm³, triclinic, space group *P*Ī, *a* = 9.7380(19) Å, *b* = 11.180(2) Å, *c* = 12.081(2) Å, *a* = 92.93(3)°, *β* = 109.48(3)°, γ = 109.87(3)°, *V* = 1145.9(4) Å³, *Z* = 2, *d*_{calcd} = 1.551 Mgm⁻³, Mo- K_a radiation (graphite-monochromated, λ = 0.71073 Å), *T* = 100 K, θ_{range} 1.97 to 30.05°. Reflections measd. 11697, indep. 6626, R_{int} = 0.0292. Final *R* indices [*I*>2 σ (*I*)]: *R*₁ = 0.0345, *wR*₂ = 0.0838.

Compound [1(AgI)₂]_n: AgI (442 mg, 1.884 mmol) was added to 1 (500 mg, 0.942 mmol) in CH₃CN (10 mL). The pale green reaction mixture was heated at 90 °C to reflux for a period of 4 h. Then half of the solvent was removed under vacuum. Subsequently, the hot reaction mixture was filtered, and the solid residue was washed with a small quantity of CH₃CN. Finally, the pale yellow product was dried under vacuum to obtain 791 mg of $[1(AgI)_2]_n$ (0.791 mmol, 84% yield). Crystals suitable for an XRD analysis were grown over a period of several weeks from concentrated DMF solutions. C₂₆H₅₀Ag₂I₂N₁₂ (1000.30): calcd. C 31.22, H 5.04, N 16.80; found C 31.05, H 4.89, N 16.57. ¹H NMR (199.92 MHz, CDCl₃): δ = 2.76 (s, 48 H, CH₃), 5.37 (s, 2 H, Ar_H) ppm. ¹³C NMR $(100.55 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 40.06 \text{ (CH}_3)$, 111.41, 136.16, 162.30 ppm. IR (CsI): $\tilde{v} = 2927$ (m), 1536 (s, C=N), 1420 (s), 1383 (s), 1263 (m), 1178 (m), 1064 (m), 1021 (vs), 922 (w), 888 (s), 866 (m), 774 (m), 711 (m), 572 (m), 474 (w), 428 (w) cm⁻¹. MS-FAB⁺: m/z(%): 486.4 (25) $[1 - NMe_2]^+$, 531.5 (100) $[1 + H]^+$, 637.4 (0.3) $[1 + H]^+$ $Ag]^{+}$, 659.4 (0.6) $[1 + I]^{+}$, 765.2 (0.2) $[1 + Ag + I]^{+}$. UV/Vis (CH₃CN, $c = 2.62 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε in L mol⁻¹ cm⁻¹) = 225 (28738), 273 (17499), 329 (11595), 378 (9384), 421 (7606) nm. Crystal data for $C_{13}H_{25}AgIN_6 \cdot 2DMF$: $M_r = 646.35$, $0.11 \times 0.07 \times 0.03$ mm³, monoclinic, space group $P2_1/c$, a =11.754(5) Å, b = 22.070(9) Å, c = 10.787(5) Å, $\beta = 110.644(6)^{\circ}$, V = 2618.5(19) Å³, Z = 4, $d_{\text{calcd.}}$ = 1.640 Mg m⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 2.07$ to 32.21°. Reflections measd. 66037, indep. 8826, $R_{\rm int} = 0.0508$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0283$, $wR_2 = 0.0556$.

Compound [1(Ag₄Cl₆)]_n: AgCl (270 mg, 1.88 mmol) was added to a solution of 1 (200 mg, 0.377 mmol) in CH₃CN (12 mL). The deep green solution was stirred at room temp. for a period of 3 h. Subsequently, the solvent was removed under vacuum and the residue was redissolved in CHCl₃ (<M;>30 mL). The dinuclear coordination compound [1(AgCl)₂] precipitated after approximately 1 h at 4 °C and was separated by filtration; yield 70 mg (0.086 mmol, 23%). The filtrate was kept at room temp. for several days until complete evaporation of the CHCl₃ solvent, during which time brown-red crystals of $[1(Ag_4Cl_6)]_n$ were formed. This product was washed several times with CH₂Cl₂; yield 133 mg (0.08 mmol, 21%). The third product, (1)Cl₂, dissolved in the CH₂Cl₂ phases. The solution was stored for 24 h at a temperature of 4 °C. Dark green crystals of (1)Cl₂ formed (25 mg, 0.042 mmol, 11%). Analysis for [1(Ag₄Cl₆)]_n: C₃₀H₅₄Ag₄Cl₁₈N₁₂ (1652.45): calcd. C 21.81, H 3.29, N 10.17; found C 21.99, H 3.32, N 10.26. ¹H NMR (400 MHz, CDCl₃): δ = 3.18 (s, 48 H, CH₃), 5.00 (s, 2 H, Ar_H) ppm. Due to low solubility in CDCl₃ and decomposition in other solvents (see discussion), it proved impossible to obtain reliable ¹³C NMR spectroscopic data for this product. IR (CsI): $\tilde{\nu}$ = 2929, 1609, 1524, 1494, 1468, 1395, 1324, 1307, 1263, 1227, 1170, 1139, 1062, 1022, 898, 780, 738, 694, 595 cm⁻¹. UV/Vis (CH₃CN, c = $3.2 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε in $\text{L mol}^{-1} \text{ cm}^{-1}$): 217 (47535), 293 (18150), 425 (28900) nm. MS-ESI⁺ (MeOH): m/z = 265.3 (100) $[1]^{2+}$, 319.0 (2) $[1 + Ag]^{2+}$, 408.2 (1) $[1 + 2Ag + 2Cl]^{2+}$, 530.3 (30) $[1]^+$. MS-FAB⁺: m/z (%) 531.7 (100) $[1 + H]^+$, 638.1 (8) $[1 + Ag]^+$.

Crystal data for $[1(Ag_4Cl_6)]$ ·4CHCl₃: $C_{15}H_{27}Ag_2Cl_9N_6$, $M_r = 826.22, 0.35 \times 0.25 \times 0.25 \text{ mm}^3$, monoclinic, space group $P2_1/c$, a = 20.956(4) Å, b = 11.688(2) Å, c = 23.445(5) Å, $\beta = 92.82(3)^\circ$, V = 5735.5(19) Å³, Z = 8, $d_{calcd.} = 1.914$ Mg m⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 1.95 to 33.11°. Reflections measd. 42828, indep. 21709, $R_{int} = 0.0707$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0523$, $wR_2 = 0.1190$. Crystal data for $[1(Ag_4Cl_6)]$ ·2CH₂Cl₂: $C_{14}H_{27}Ag_2Cl_5N_6$, $M_r = 672.41$, $0.30 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P2_1/n$, a = 13.058(3) Å, b = 11.688(2) Å, c = 15.697(3) Å, $\beta = 107.03(3)^\circ$, V = 2290.7(8) Å³, Z = 4, $d_{calcd.} = 1.950$ Mg m⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.50 to 31.14°. Reflections measd. 14081, indep. 7282, $R_{int} = 0.0346$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0399$, $wR_2 = 0.0987$.

Decomposition of [1(Ag_4Cl_6)]_n: Compound $[1(Ag_4Cl_6)]_n$ (43.8 mg) was dissolved in MeOH (3 mL). Formation of a white precipitate was observed over a period of several days. The solution was filtered and the pale yellow powder dried under vacuum. It was dissolved in aqueous NH₃, precipitated upon addition of aqueous HNO₃, and was identified as AgCl. The green filtrate contained (1)Cl₂ (15.9 mg).

Compound [1(AgCl)₂]: AgCl (54 mg, 0.377 mmol) was added to a solution of 1 (100 mg, 0.188 mmol) in toluene (10 mL). The reaction mixture was stirred for 3 h at a temperature of 90 °C, leading to a white precipitate of [1(AgCl)₂]. This precipitate was filtered, washed with small quantities of toluene and dried; yield 120 mg (0.147 mmol, 78%). C₃₃H₅₈Ag₂Cl₂N₁₂ [M + C₇H₈] (909.54): calcd. C 43.58, H 6.43, N 18.48; found C 42.96, H 6.38, N 18.31. ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 2.76$ (48 H, CH_3), 5.44 (2 H, Ar_H) ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ = 40.2 (CH₃), 111.6, 135.5, 162.7 ppm. IR (CsI): v = 2927, 1546, 1483, 1420, 1386, 1264, 1234, 1179, 1144, 1060, 1023, 890, 827, 790, 709, 572 cm⁻¹. UV/Vis (CH₃CN, $c = 9.90 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε in L mol⁻¹ cm⁻¹) = 218 (18908), 290 (9207), 426 (13793) nm. MS-FAB⁺: m/z (%) = 531.5 H]⁺, 781.3 (0.6) [1 + 2Ag + Cl]⁺, 816.2 (0.5) [M]⁺. Crystal data for $C_{33}H_{57}Ag_2Cl_2N_{12}$, $[1(AgCl)_2] \cdot C_7H_8$: $M_{\rm r}$ = 908.55. $0.25 \times 0.20 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/c$, a =13.428(3) Å, b = 7.3260(15) Å, c = 21.555(4) Å, $\beta = 107.64(3)^{\circ}$, V = 2020.7(7) Å³, Z = 2, $d_{calcd.}$ = 1.493 Mgm⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.13 to 27.92°. Reflections measd. 9491, indep. 4811, $R_{int} = 0.0334$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0351$, $wR_2 = 0.0793$.

Compound [1(AgCl)₂] Dissolved in CH₂Cl₂: Compound [1(AgCl)₂] (60 mg) was dissolved in CH₂Cl₂ (10 mL) and heated to 40 °C for several minutes. The solution turned green and formation of precipitate was observed. The solution was filtered and concentrated. Crystals of $[1(Ag_4Cl_6)]_n$ formed over a period of several days. For analytical data, see above.

Oxidation Experiments with $[1(AgBr)_2]_n$ and $[1(AgI)_2]_n$

[1(Ag₆I_{8-x}Br_x)]_n (x = 0.7): I₂ (28 mg, 0.110 mmol) was added to a solution of [1(AgBr)₂]_n (100 mg, 0.110 mmol) in CH₃CN (12 mL). The dark yellow reaction mixture was stirred at room temp. for a period of 2 h. The product precipitated over the course of the reaction as a black powder. The reaction mixture was filtered, the product washed twice with CH₃CN and dried under vacuum to yield 62 mg (0.027 mmol, 26%). Crystals of the polymer [1(Ag₆I_{8-x}Br_x)]_n (x = 0.7) suitable for an XRD analysis were obtained from CH₃CN/Et₂O or concentrated DMF solutions. C₂₉H₅₇Ag₆Br_{0.7}I_{7.3}N₁₃O₁ [M + DMF] (2233.4): calcd. C 15.60, H 2.57, N 8.15; found C 15.85, H 2.44, N 8.30. ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 3.08$ (48 H, CH₃), 5.17 (2 H, Ar_H) ppm. Low

solubility hampered the ¹³C NMR spectra. IR (CsI): $\tilde{v} = 2963$, 1669, 1615, 1528, 1492, 1465, 1393, 1324, 1303, 1263, 1169, 1095, 1025, 801, 696, 602 cm⁻¹. MS-FAB⁺: *m*/*z* (%) = 530.4 (100) [1]⁺, 609.2 (42) [1 + Br]⁺, 970.1 (5) [1 + Ag + Br + 2I]⁺. UV/Vis (CH₃CN, *c* = 2.30×10⁻⁶ molL⁻¹): λ_{max} (*ε* in Lmol⁻¹cm⁻¹) = 220 (27142), 245 (13434), 286 (13434), 427 (5277) nm. Crystal data for C₂₆H₅₀Ag₆Br_{0.7}I_{7.3}N₁₂: *M*_r = 2160.31, 0.30×0.20×0.20 mm³, monoclinic, space group *C2*/*c*, *a* = 13.695(3) Å, *b* = 14.591(3) Å, *c* = 25.807(5) Å, β = 104.85(3)°, *V* = 4984.6(17) Å³, *Z* = 4, *d*_{calcd}. = 2.879 Mgm⁻³, Mo-*K*_α radiation (graphite-monochromated, λ = 0.71073 Å), *T* = 100 K, θ_{range} 2.08 to 30.09°. Reflections measd. 35968, indep. 7226, *R*_{int} = 0.0582. Final *R* indices [*I* > 2*σ*(*I*)]: *R*₁ = 0.0571, *wR*₂ = 0.1654.

Compound $[1(Ag_5Br_4I_3)]_n$: I₂ (14 mg, 0.055 mmol) was added to a suspension of $[1(AgBr)_2]_n$ (100 mg, 0.110 mmol) in CH₃CN (12 mL). The reaction mixture was stirred at room temp. for a period of 2 h. The product (1.2 mg, 0.6 µmol, 1%) was crystallized from the reaction mixture. The white precipitate in the suspension was identified as starting reagent. C₃₂H₆₄Ag₅Br₄I₃N₁₄O₂ [M + 2DMF] (1916.61): calcd. C 20.05, H 3.37, N 10.23; found C 21.03, H 3.33, N 10.08. ¹H NMR (400 MHz, [D₆]DMSO): δ = 2.86 (s, 48 H, CH₃), 5.13 (s, 2 H, Ar_H) ppm. Low solubility hampered the ${}^{13}C$ NMR spectroscopic studies. IR (CsI): $\tilde{v} = 2927$, 1611, 1528, 1492, 1460, 1395, 1324, 1303, 1229, 1172, 1144, 1066, 1025, 896, 805, 782, 741, 696 cm⁻¹. UV/Vis (CH₃CN, $c = 9.03 \times 10^{-6} \text{ mol } \text{L}^{-1}$): λ_{max} $(\varepsilon \text{ in } \text{Lmol}^{-1} \text{ cm}^{-1}) = 213 (7453), 293 (1432), 425 (2169) \text{ nm. MS-}$ ESI⁺ (MeOH/CH₃CN): m/z (%) = 265.3 (100) [1]²⁺, 530.3 (45) $[1]^+, 610.1 (6.9) [1 + H + Br]^+, 689.1 (2) [1 + H + 2Br]^+, 1398.7$ (1) $[1 + H + 5Ag + Br + 2I]^+$, MS-ESI⁻ (MeOH/CH₃CN): m/z (%) = 156.1 (32) [Ag + Br + I]⁻, 863.2 (7) [1 + 2I + Br]⁻. Crystal data for $C_{28}H_{53}Ag_5Br_4I_3N_{13}$: $M_r = 1811.49, 0.25 \times 0.18 \times 0.18 \text{ mm}^3$, triclinic, space group $P\bar{1}$, a = 10.154(2) Å, b = 12.962(3) Å, c =20.173(4) Å, $a = 91.13(3)^\circ$, $\beta = 101.84(3)^\circ$, $\gamma = 109.83(3)^\circ$, $V = 109.83(3)^\circ$ 2433.0(11) Å³, Z = 2, $d_{calcd.} = 2.473 \text{ Mg m}^{-3}$, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 2.06$ to 29.99°. Reflections measd. 25403, indep. 13998, $R_{\text{int}} = 0.0429$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0525$, $wR_2 = 0.1264$.

Compound 1(AgI₃): I₂ (26.6 mg, 0.105 mmol) was added to a suspension of $[1(AgI)_2]_n$ (210 mg, 0.21 mmol) in CH₃CN (12 mL). The reaction mixture was stirred at room temp. for a period of 2 h. Then the reaction mixture was filtered, the solvent removed under vacuum, and the residue redissolved in CHCl₃ (<M;>10 mL) and filtered. The concentrated solution was kept at 4 °C overnight, while brown crystals of 1(AgI₃)·2CHCl₃ formed; yield 29 mg (0.023 mmol, 11%). Crystals suitable for an XRD analysis were obtained from concentrated CH₃CN solution. C₂₈H₅₂AgCl₆I₃N₁₂ (1258.09): calcd. C 26.73, H 4.17, N 13.36; found C 26.98, H 4.27, N 14.40. ¹H NMR (400 MHz, CD₃CN): δ = 2.88 (48 H, CH₃), 5.16 $(2 \text{ H}, \text{Ar}_{\text{H}})$ ppm. ¹³C NMR (100 MHz, CD₃CN): δ = 41.46, 103.97, 157.66, 168.04 ppm. IR (CsI): v = 2933, 1602, 1529, 1496, 1465, 1424, 1396, 1380, 1307, 1263, 1231, 1159, 1070, 1018, 898, 882, 845, 813, 781, 757, 737, 685, 620, 584, 540, 516, 452 $\rm cm^{-1}.~UV/Vis$ (CH₃CN, $c = 1.2 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε in $\text{Lmol}^{-1} \text{cm}^{-1}$) = 209 (25981), 245 (18053), 293 (6127), 426 (10216) nm. MS-ESI+ (CH₃CN): m/z (%) = 265.3 (100) [1]²⁺, 328.2 (13) [1 + I]²⁺, 530. 3 (16.9) [1]⁺, 657.2 (3) [1 + I]⁺, 891.1 (5) [1 + AgI₂]⁺, 1018.8 (1) [1 + AgI₃]⁺. MS-ESI⁻ (CH₃CN): *m*/*z* (%) = 361.7 (100) [Ag + 2I]⁻, 489.0 (1) $[Ag + 3I + H]^{-}$. Crystal data for C₂₆H₅₀AgI₃N₁₂: $M_r = 1019.35$, $0.45 \times 0.40 \times 0.40$ mm³, monoclinic, space group C2/c, a = 13.729(3) Å, b = 14.841(3) Å, c = 17.986(4) Å, $\beta = 94.13(3)^{\circ}$, V = 3655.2(13) Å³, Z = 4, $d_{calcd.}$ = 1.852 Mgm⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{\text{range}} 2.27$

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to 33.12°. Reflections measd. 13682, indep. 6934, $R_{int} = 0.0239$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0278$, $wR_2 = 0.0590$.

Compound 1(DDQ)₂: From treatment of $[1(AgBr)_2]_n$ with 2 equiv. DDQ: DDQ (50 mg, 0.220 mmol) was added to a solution of [1(AgBr)₂] (100 mg, 0.110 mmol) in CHCl₃ (12 mL). The brownred reaction mixture was stirred at room temp. for a period of 2 h. Then the solvent was removed under vacuum and the crude product redissolved in acetone (20 mL). By cooling the acetone solution to 4 °C, 1(DDQ)₂ (73 mg) was obtained the next day as black crystalline solid (0.074 mmol, 67%). Crystals suitable for an XRD analysis were obtained from CH₃CN/Et₂O. C₄₂H₅₀Cl₄N₁₆O₄ (984.76): calcd. C 51.23, H 5.12, N 22.76; found C 51.02, H 5.12, N 22.08. ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 3.07$ (48 H, CH_3), 5.17 $(2 \text{ H}, \text{Ar}_{\text{H}})$ ppm. ¹³C NMR (100 MHz, CD₃CN): δ = 41.75, 104.69, 157.61, 168.03 ppm. IR (CsI): v = 2943, 2214, 1653, 1625, 1559, 1512, 1468, 1402, 1316, 1287, 1230, 1191, 1170, 1143, 1066, 1018, 886, 787, 753, 713, 516, 476 cm⁻¹. UV/Vis (CH₃CN, c = $4.69 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε in $\text{Lmol}^{-1} \text{cm}^{-1}$) = 222 (21411), 301 (8228), 415 (4524) nm. MS-FAB+: m/z (%) 530.5 (100) [1]+, 758.6 (8) [1 + DDQ]⁺. MS-FAB⁻: m/z (%) 228.1 (100) [DDQ]⁻. Crystal data for $1(DDQ)_2 \cdot 2CH_3CN$: $C_{46}N_{56}Cl_4N_{18}O_4$, $M_r = 1066.89$, $0.40 \times 0.40 \times 0.35 \text{ mm}^3$, triclinic, space group $P\bar{1}$, a = 7.7080(15) Å, b = 12.654(3) Å, c = 13.100(3) Å, $a = 94.95(3)^{\circ}$, $\beta = 97.28(3)^{\circ}$, $\gamma = 12.654(3)^{\circ}$ 92.23(3)°, V = 1261.1(5) Å³, Z = 1, $d_{calcd.} = 1.405$ Mg m⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.36 to 30.00°. Reflections measd. 13426, indep. 7291, R_{int} = 0.0549. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0504$, $wR_2 = 0.1077$.

Compound 1(DDQ)₂: From treatment of $[1(AgI)_2]_n$ with 2 equiv. DDQ: The procedure was similar to the one described above. Compound $[1(AgI)_2]_n$ (100 mg, 0.100 mmol) and DDQ (45 mg, 0.200 mmol) were used; yield 63 mg (0.064 mmol; 64%). For analysis, see above.

Compound [1(Ag₆I₈)]_{*n*}: From treatment of [1(AgI)₂]_{*n*} with 1 equiv. TCQ: TCQ (24.5 mg, 0.100 mmol) was added to a suspension of [1(AgI)₂]_{*n*} (100 mg, 0.100 mmol) in CH₃CN (12 mL). Then the reaction mixture was stirred at room temp. for a period of 2 h. After filtration the precipitate was washed twice with CH₃CN and dried under vacuum to yield 65 mg of product (0.030 mmol, 30%). Crystals were grown from the reaction mixture or concentrated DMF solutions. $C_{26}H_{50}Ag_6I_8N_{12}$ (2193.20): calcd. C 14.24, H 2.30, N 7.66; found C 14.79, H 2.42, N 7.81. Further analysis see above.

Compound $[1(Ag_6I_8)]_n$: From treatment of $[1(AgI)_2]_n$ with 2 equiv. TCNQ: TCNQ (16.3 mg, 0.80 mmol) was added to a suspension of $[1(AgI)_2]_n$ (40 mg, 0.040 mmol) in CH₃CN (12 mL). Then the reaction mixture was stirred at room temp. for a period of 2 h. After filtration the precipitate was washed twice with CH₃CN and dried under vacuum to yield 14 mg of product (0.06 mmol, 16%). Crystals were grown from reaction mixture or concentrated DMF solution. For analysis, see above.

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed on top of a glass capillary. Measurements were made with a Nonius-Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo- K_a radiation. The temperature was set to 100 K. The data collected were processed with the standard Nonius software.^[17] All calculations were performed with the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.^[18,19] Graphical handling of the structural data during solution and refinement was performed with XPMA.^[20] Atomic coordinates and anisotropic thermal parameters

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of non-hydrogen atoms were refined by full-matrix least-squares calculations.

CCDC-844519 [for (1)Cl₂], -844518 [for (1)Br₂·4MeOH], -844824 [for $1(Ag_6I_8)]_n$, -844522 [for $1(Ag_6I_8)\cdot 2DMF]_n$, -844514 [for $1(AgBr)_2\cdot 4CHC_3]_n$, -844524 [for $1(AgI)_2\cdot 4DMF]_n$, -844523 [for $1(Ag_4CI_6)\cdot 4CHCI_3]_n$, -844520 [for $1(Ag_4CI_6)\cdot 2CH_2CI_2]_n$, -844521 [for $1(AgCI)_2\cdot C_7H_8$, -844525 {for $[1(Ag_6I_8_xBr_x)]_n$ (x = 0.7)}, -844517 [for $1(Ag_5Br_4I_3)]_n$, -844515 [for $1(AgI_3)$] and -844516 [for $1(DDQ)_2\cdot 2CH_3CN]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Remission spectra of $[1(AgBr)_2]_n$ and $[1(AgI)_2]_n$ and photos of $[1(AgBr)_2]_n$ before and after heating to a temperature of 650 °C.

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