

CHEMISTRY A European Journal





Supported by ACES



A novel family of polyiodo-bromoantimonate(III) complexes: cation-driven self-assembly of photoconductive metal-polyhalide frameworks

Sergey A. Adonin,*^{[a] [b]} Liubov I. Udalova,^{[a] [b]} Pavel A. Abramov,^{[a] [b]} Alexander S. Novikov,^[c] Irina V. Yushina,^[a] Ilya V. Korolkov,^{[a] [b]} Evgeniy Yu. Semitut,^[a] Tatiyana A. Derzhavskaya,^[d] Keith J. Stevenson,^[e] Pavel A. Troshin,^{[d] [e]} Maxim N. Sokolov^{[a] [b]} and Vladimir P. Fedin^{[a] [b]}

Abstract: In presence of different cations, reactions of $[SbBr_6]^{3^{-}}$ and I_2 result in a new family of diverse supramolecular 1D polyiodidebromoantimonate networks. Coordination number of Sb, as well as geometry of assembling $\{I_x\}^{n^{-}}$ polyhalide units, can vary, resulting in unprecedented structural types. The nature of I…Br interactions was studied by DFT calculations; estimated energy values are 1.6–6.9 kcal/mol. Some of the compounds showed strong photoconductivity in thin films, suggesting multiple feasible applications in optoelectronics and solar energy conversion.

Introduction

Although the first polyhalides were discovered decades ago, this field of chemistry has been progressing, resulting in an astonishing variety of compounds, often with promising properties,¹⁻³ and it keeps providing the chemical community with unexpected and fascinating results. The most recent advances were achieved in the area of non-iodide polyhalides, for example, synthesis and theoretical studies of enhanced polybromide frameworks⁴⁻⁶ and polychlorides;⁷ the latter are of special interest due to the clearly decreasing ability to form polyhalides in the I > Br > Cl >> F row. However, despite the general progress in this field, it can be noted that the polyhalide *metal complexes* remain incomparably less explored. For the all-polyhalide complexes, single examples are known for polyiodides⁸⁻¹¹ and polybromides.¹²⁻¹⁷ Coordination of mixed

[a]	Dr. S.A. Adonin, Ms. L.I. Udalova, Dr. P.A. Abramov, Ms. I.V.
	Yushina, Dr. I.V. Korolkov, Dr. E.Yu. Semitut, Prof. Dr. M.N.
	Sokolov, Prof. Dr. V.P. Fedin
	Nikolaev Institute of Inorganic Chemistry SB RAS
	630090 Lavrentieva St. 3, Novosibirsk, Russia.
	E-mail: adonin@niic.nsc.ru
[b]	Dr. S.A. Adonin, Ms. L.I. Udalova, Dr. P.A. Abramov, Dr. I.V.
	Korolkov, Prof. Dr. M.N. Sokolov, Prof. Dr. V.P. Fedin
	Novosibirsk State University
	630090 Pirogova St. 2, Novosibirsk, Russia
[c]	Dr. A.S. Novikov
	Institute of Chemistry
	Saint Petersburg State University
	199034 Universitetskaya Nab. 7-9, Saint Petersburg, Russia
[d]	Dr. T.A. Derzhavskaya, Prof. Dr. P.A. Troshin
	Institute for Problems of Chemical Physics RAS
	142432 Semenov ave. 1, Chernogolovka, Russia
[e]	Prof. Dr. K.J. Stevenson, Prof. Dr. P.A. Troshin
	Skolkovo Institute of Science and Technology
	121205 Nobelya St. 3, Moscow, Russia

Supporting information for this article is given via a link at the end of the document.

polyhalides ((Brl₂), (ClBr₂)) was reported mostly for heteroligand complexes. $^{18\text{-}21}$

Very recently, we discovered a series of Bi(III) polybromide complexes, featuring a remarkable structural diversity and containing $\{Br_x\}$ units of variable nuclearity (up to 9).²² In all cases, the compounds were obtained by a straightforward method: " $[BiBr_6]^{3-}$ + Br₂ + (cation)Br_x + HBr". Geometry of the cation plays crucial role, promoting formation of a particular type of 0D, 1D or 2D-anion. Analyzing the earlier publications, we noticed that the studies of corresponding reactions with [SbBr₆]³⁻ were performed by Lawton et al. decades ago. The authors found that these reactions are also cation-dependent, but the nature of possible products may be here even more diverse due to the ability of Sb (III) to be oxidized by Br2 into [SbBr6].23-25 Therefore, there appear six possible combinations: Sb(III), Sb(V) or mixed-valent complex with or without polybromide units in the structure. Although these results are very inspiring and interesting from the point of view of chemistry of both p-block metals and halogens, and this work can be expanded, we could not find consequent studies in this field. Attempting to fill this gap, we decided to investigate behavior of bromoantimonate (III)/HBr systems in presence of I₂ assuming that: 1) Sb(III) cannot be oxidized into Sb(V) by I_2 , 2) mixed bromide/polyiodide complexes may form, which, considering the enhanced ability of iodine to build extended polyhalide units, might attain higher dimensionality, and 3) these compounds might display narrow optical band gaps, which are attractive for designing iodometalate-based solar cells.26-29

In this work, we present a new family of polymeric polyiodo(bromo)antimonates (III) belonging to four different structural types, exemplified by $(Me_4N)_3\{\alpha-[Sb_2Br_9](l_2)\}$ (1), (4-MePyH)₃ $\{\beta-[Sb_2Br_9](l_2)\}$ (2), and $(BPE)\{[SbBr_5](l_2)\}$ (3) (BPE = N,N-bis-(Py)ethane cation), as well as their optical features (photoconductivity) and theoretical insights into the nature and energy of I \cdots Br contacts.

Results and Discussion

For preparation of **1-3**, we have applied the approach developed for synthesis of polybromometalates earlier:²² HBr solutions of bromides of various cations were added to the HBr solutions containing $[SbBr_6]^{3-}$ and dissolved I_2 . Considering lesser hydrolytic stability of $[SbBr_6]^{3-}$ in comparison with $[BiBr_6]^{3-}$, higher concentrations of HBr were used (see Experimental Section). In some cases, formation of crystalline products succeeded only if resulting mixtures were cooled (see below). In total, over 20 cations were tested; the list of experiments is given in SI. It can be seen that in many cases there form crystalline solids of quality insufficient for XRD. The dark color itself indicates the

presence of polyiodide, but not haloantimonate (in several experiments, we isolated polyiodide or polyiodobromide salts of corresponding organic cations).

Compounds 1 and 2 reveal the same composition of the anionic part, as well as certain structural similarity. In both cases, the main "building blocks" are binuclear {Sb₂Br₉} (two {SbBr₆} octahedra sharing one face) which were found in several bromoantimonates (III) earlier;³⁰⁻³² the average Sb-Br_{term} and Sb- μ_2 -Br bonds are similar to those found in $[Sb_2Br_9]^{3-}$ salts (2.633(1), 3.041(1) and 2.666(1), 3.060(1) Å in 1 and 2, respectively). The structural feature of both 1 and 2 is the presence of "trapped" $\{I_2\}$ which participate in specific interactions with the terminal bromide ligands of {Sb₂Br₉}, thus forming one-dimensional chains. The Brterm-I distances are 3.145(1) in 1 and 3.461(1) Å in 2, being clearly less than the sum of Bondi's (the shortest) van der Waals radii for Br and I (3.81 Å). As in the case of the Bi(III) polybromides,²² this justifies proposing the existence of specific supramolecular contacts between these units. The difference between the $\{[Sb_2Br_9](I_2)\}$ substructures in 1 and 2 is the mutual orientation of $\{I_2\}$ and {Sb₂Br₉}, resulting in two various types of the chain structure, which might be described as transoid (1) and cisoid (2) isomers of the polymeric chain (Figure 1). The cisoid binding mode was found earlier in polybromide complexes of Bi(III)²², and in the single known example of polybromoantimonate (III), while the transoid mode has not been reported before.



<u>Figure 1.</u> Interactions between $\{Sb_2Br_3\}$ and I_2 units in 1 (top) and 2 (bottom). Sb blue, Br olive-green, I purple, Br…I contacts dashed

Another structural type of polyiodo(bromoantimonate) was found in **3**, possessing a number of interesting features. First, the coordination number of Sb(III) is lower: each Sb is surrounded by five bromide ligands, forming a severely distorted tetragonal pyramid. All the Sb-Br distances are non-equal: the unusually short one (2.5347(6) Å) corresponds to the Br ligand located trans to the lone pair. Three Sb-Br bonds fit within the usual range (2.6375(5)-2.8334(5) Å). The most remote Br ligand (Sb-Br = 2.9784(5) Å) is connected with {I₂} unit. The I···Br distance is 2.9534(5) Å (Br-I-I = 174.6°), and this observation allows us postulating the presence of rare BrI₂- ligand. According to the CSD data, in both known cases where coordination of {BrI₂} was observed, the geometry of this fragment was comparable (Br-I = 2.855-2.948 and 2.913 Å, Br-I-I = 174.48-177.50 and 175.84° for Cu³³ and Pd,²⁰ respectively). Each {BrI₂} unit has longer contacts with one of the Br ligands of another {SbBr₄(BrI₂)} moiety (I···Br = 3.621(1) Å), forming a linear chain (Figure 2). The distances between {I₂} and Sb in neighboring chains exceed the sum of van der Waals radii (4.04 vs 4.186(1)-4.235(1)Å).



Figure 2. One-dimensional chains in 3. Sb blue, Br olive-green, I purple, I…Br contacts dashed

Topological analysis of the electron density distribution within the formalism of Bader's theory (QTAIM method)³⁴ is an efficient tool for the studies of various non-covalent interactions in different complexes.³⁵⁻³⁸ Details of calculations for **1-3** are summarized in Table 4S (SI). To visualize the non-covalent interactions, reduced density gradient (RDG) analysis was carried out;³⁹ RDG isosurfaces were plotted (Figures 4 and 5). In all cases, QTAIM analysis demonstrates the presence of appropriate bond critical points (BCPs) (3, –1) for different noncovalent interactions (Table 4S).



Figure 4. Contour line diagrams of the Laplacian distribution ∇²ρ(r), bond paths and selected zero-flux surfaces (left) and RDG isosurfaces (right) referring to different non-covalent interactions in 1 (I···Br – top) and 3 (bifurcated I···Sb···I – bottom). Bond critical points (3, –1) blue, nuclear critical points (3, –3) pale brown, ring critical points (3, +1) orange. Length units – Å, RDG isosurface values are given in Hartree.

WILEY-VCH

10.1002/chem.201802100



Figure 5. Contour line diagram of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths and selected zero-flux surfaces (left) and RDG isosurface (right) referring to I···Br non-covalent interactions in **2**. Bond critical points (3, -1) blue, nuclear critical points (3, -3) pale brown. Length units – Å, RDG isosurface values are given in Hartree.

Two types of short halogen–halogen contacts are usually discussed in the literature (see figure in SI).^{40,41} Type I is believed to depend on the effects of crystal packing, while type II is due to a classic halogen bonding (XB) (a halogen atom with a 90° angle provides its lone pair for interaction and the other one provides its σ -hole). The non-covalent interactions I…Br in **1**, **2**, and **3** can be attributed as type I contacts.

The low magnitude of the electron density (0.004–0.033 Hartree), positive values of the Laplacian (0.014-0.061 Hartree), and close-to-zero energy density (-0.003-0.001 Hartree) in these BCPs are typical for non-covalent interactions. We extracted the energies of these contacts according to the previously proposed procedures,^{42,43} and can state that strength of these noncovalent interactions varies from 0.6 to 6.9 kcal/mol. The balance between the Lagrangian kinetic energy G(r) and potential energy density V(r) at the BCPs (3, -1) reveals the nature of these interactions: if the ratio -G(r)/V(r) > 1 is satisfied, then the interaction is purely non-covalent, if the -G(r)/V(r) < 1, there is some covalent component.⁴⁴ Based on this criterion we state that many contacts listed in Table 4S allow some covalent contribution. The nature of different non-covalent interactions in 1-3 was also analyzed based on the Wiberg bond indices computed by using the natural bond orbital (NBO) partitioning scheme.⁴⁵ The values of the Wiberg bond indices for purely noncovalent contacts I. Br in 2; I. Br and Sb. I in 3 are relatively small (0.02-0.03), which also confirms the electrostatic nature of these weak interactions, whereas for other contacts with some covalent contributions (see Table 4S) the values of the Wiberg bond indices are noticeable (0.11-0.22).

According to the PXRD data (see SI), **1** and **3** can be isolated in pure form (for **2**, formation of unidentified by-products persists), making detailed investigation of bulk samples possible. Preliminary estimation of the optical band gaps for **1** and **3** resulted in values below 1.5 eV (see SI), making them promising candidates for photovoltaic applications. An additional argument in favor of their feasible practical use is their decent thermal stability, which was studied by TGA (see SI): decomposition related to the loss of diiodine starts at 100-150°C. Additionally, we have recorded Raman spectra (see SI); in all cases, those are consistent with symmetries of corresponding polyhalide

units.⁴⁶ In order to reveal the potential of the designed compounds as electronic materials, their thin films are incorporated in the lateral two-electrode device geometry (Figure 6a) and probed for existence of any semiconductor behavior and photoconductivity effects. It should be emphasized that growing thin films was a very challenging task considering the fact that **1**-**3** can hardly be solubilized in organic or inorganic solvents without complete degradation. Nevertheless, we found that solution of Me₄NBr, SbBr₃ and I₂ (I₂ should be taken in 3-4 fold excess compared to the stoichiometric amount) in anhydrous CH₂Cl₂ is rather stable and can be drop-casted to produce thin crystalline film of **1**. Interestingly, spin-coating did not work resulting in the formation of iodine-free complex antimony bromides.

Figure 6b shows the current-voltage characteristics of the lateral two-electrode device with the active film of **1** measured in the dark and under illumination with the violet light (405 nm, ~70 mW/cm², diode laser). One can clearly see that the current increases by almost two orders of magnitude under illumination (see also log plot in SI), thus manifesting relatively strong photoconductivity effect. This behavior suggests that **1** represents a promising semiconductor material for multiplication-type photodetectors and, probably, also for "perovskite-inspired" solar cells using complex metal halides as active layer materials. Further research in that direction as well as exploration of characteristics of **2** and **3** is currently in progress.



Figure 6. Schematic layout of the lateral two-electrode device with compound 1 used as semiconductor (a). Current-voltage characteristics of the device measured in dark and under violet light illumination (405 nm, 70 mW/cm²) given in linear scale (b).

Conclusions

10.1002/chem.201802100

Several points can be highlighted in conclusion. First, the simple combination "dihalogen + hydrohalic acid" by itself represents a potent virtual dynamic library which is applicable in inorganic synthesis, resulting in cation-driven formation of numerous polyhalides of different dimensionality. Considering the main advantage of this system - simplicity of preparation, especially in comparison with ionic liquids which are currently widely used for the preparation of polyhalides - it certainly deserves to be exploited further. Second, unlike bismuth, Sb adopts variable coordination environment, adjusting to the crystal packing. This feature appears to be due to the more pronounced activity of the lone pair at Sb(III); although there are examples of square pyramidal Sb compounds^{47,48} and such behaviour was reported for haloantimonates (III), it is not very common.⁴⁹ Also, this feature was not yet observed in corresponding polybromides of Sb(V) reported by us recently.⁵⁰ Finally, increased dimensionality of the designed complexes is manifested in their semiconductor properties (similar observations were made for Pb(II)⁵¹ and Bi(III)⁵² polyiodide hybrids) and strong photoconductivity effects, featuring multiple potential applications in electronics and photovoltaics.

Experimental Section

General remarks. All experiments were carries out in air. BPE and 4-EtBPE dibromides were obtained by reactions of pyridine or 4-ethylpyridine with 1,2-dibromoethane (CH₃CN, stirring, 12 h); purity was confirmed by ¹H NMR and element analysis.

Preparation of 1-3. For **1**, 50 mg (0.17 mmol) of Sb₂O₃ were dissolved in 7 ml of concentrated HBr. Then, 44 mg of I₂ were added; solution was stirred for 1 h resulting in complete dissolution of I₂. Then, solution of Me₄NBr (44 mg, 1.1x excess) in 2 ml of HBr was added and the mixture was kept at 6°C for 12 h, resulting in formation of dark crystalline precipitate. For **2–3**, procedure was similar, using 4-MePy (28 mcl) in 2 ml HBr (**2**) or 88 mg of I₂ (11 ml HBr) and BPEBr₂ (118 mg in 4 ml) (**3**). In all cases, yield was 81-85% (for **2** – estimated). Data of element analysis are given in SI.

Fabrication of the lateral two-electrode device with compound 1. Glass slides (15x15 mm) were cleaned first in the base piranha solution (25% aqueous NH_3 + 30% H_2O_2 , 4:1), then washed with deionized water, dried with a stream of nitrogen and further treated with oxygen plasma for 7 min. Gold electrodes (200 nm) were deposited by thermal evaporation in high vacuum (10-6 mbar) through the shadow mask defining the device configuration: channel length of 80 µm and width of 2 mm. Each glass slide had 4 pairs of electrodes. A solution of Me₄NBr (63.9 mg), SbBr₃ (100 mg) and I₂ (125 mg) in 1.0 mL of anhydrous CH₂Cl₂ was prepared by stirring all components together at room temperature inside MBraun glove box. The obtained solution was filtered through 0.45 µm PTFE syringe filter (no visible precipitate detected in the filter) and dropcasted above the channels between the gold electrodes. The solvent and excess of I2 were evaporated at room temperature inside the glove box leaving dark-red crystalline films of 1 (confirmed by EDX). The yield of the working devices was ca. 25% as revealed by current-voltage measurements in dark using Keithley 2612A instrument. Some devices were showing zero currents (missing contact between the material and the electrodes), while others were shorted probably due to partial dissolution of gold in the drop-casted solution. The illumination for the measurements was provided by violet diode laser (405 nm, ~70 mW/cm²) operated with Advantest 6240A source-measurement unit. All devices degraded completely under storage inside the glove box overnight, which was accompanied by the color change of the active films from dark-red to light-yellow suggesting decomposition of the polyiodide-bromoantimonate with the formation of conventional Sb(III) halides. Devices also showed noticeable degradation after each successive measurement suggesting that the active material is sensitive to light and/or electric field.

Details of X-ray Diffractometry and computational details are given in SI.

Acknowledgements

This work has been supported within the Skoltech-MIT Next Generation Program. ASN also thanks Russian Foundation for Basic Research (16-33-60063 – theoretical studies). SAA thanks the President Grant Council for a personal research fellowship. NIIC part of team thanks Federal Agency for Scientific Organizations for support as well.

Keywords: polyhalide • halometalate • antimony • photoconductivity • DFT calculations

- [1] P.H. Svensson, L. Kloo, *Chem. Rev.* **2003**, *103*, 1649
- [2] H. Haller, S. Riedel, Z. Anorg. Allg. Chem. 2014, 640, 1281
 [3] P. Deplano, J.R. Ferrar, M.L. Mercuri, E.F. Trogu, Coord. Chem. Rev.
- 1999, 188, 71
 [4] M. Wolff, A. Okrut, C. Feldmann, *Inorg. Chem.* 2011, 50, 11683
- [5] H. Haller, M. Ellwanger, A. Higelin, S. Riedel, Z. Anorg. Allg. Chem. 2012, 638, 553
- K. Sonnenberg, P. Pröhm, S. Steinhauer, A. Wiesner, C. Müller, S. Riedel, Z. Znorg. Allg. Chem. 2017, 643, 101
- [7] R. Brückner, H. Haller, S. Steinhauer, C. Müller, S. Riedel, Angew. Chem. Int. Ed. 2015, 54, 15579
- [8] P.H. Svensson, L. Kloo, *Inorg. Chem.* 1999, **38**, 3390
- [9] P.H. Svensson, J. Rosdahl, L. Kloo, Chem. Eur. J. 1999, 5, 305
- [10] T.A. Shestimerova, N.A. Yelavik, A.V. Mironov, A.N. Kuznetsov, M.A. Bykov, A.V. Grigorieva, V.V. Utochnikova, L.S. Lepnev, A.V. Shevelkov, Inorg. Chem. 2018, 57, 4077
- [11] T.A. Shestimerova, N.A. Golubev, N.A. Yelavik, M.A. Bykov, A.V. Grigorieva, Z. Wei, E.V. Dikarev, A.V. Shevelkov, Gryst. Growth Des. 2018, 18, 2572
- [12] M. Berkei, J.F. Bickley, B.T. Heaton, A. Steiner, Chem. Commun. 2002, 2180
- [13] D. Schneider, O. Schuster, H. Schmidbaur, Dalton Trans. 2005, 1940
- [14] B. Lehnis, J. Straehle, Z. Naturforsch. B: Chem. Sci. 1981, 12, 1504
- [15] A. Okrut, C. Feldmann, Inorg. Chem. 2008, 47, 3084
- [16] R. Siepmann, H.G. von Schnering, Z. Anorg. Allg. Chem. 1968, 357, 289
- [17] D. Hausmann, C. Feldmann, Inorg. Chem. 2016, 55, 6141
- [18] D. Serra, P. Cao, J. Cabrera, R. Padilla, F. Rominger, M. Limbach, Organometallics 2011, 30, 1885
- [19] J.-P. Cloutier, B. Vabre, B. Moungang-Soume, D. Zargarian, Organometallics 2015, 34, 133
- [20] M.T. Johnson, Z. Dzolis, M. Cetina, O.F. Wendt, L. Ohrstrom, K. Rissanen, Cryst. Growth Des. 2012, 12, 362
- [21] V.Yu. Kotov, N.P. Simonenko, A.B. Ilyukhin, Mendeleev Commun. 2017, 27, 454
- [22] S.A. Adonin, I.D. Gorokh, D.G. Samsonenko, M.N. Sokolov, V.P. Fedin, *Chem. Commun.* 2016, **52**, 5061

- [23] S.L. Lawton, D.M. Hoh, R.C. Johnson, A.S. Knisely, *Inorg. Chem.* 1973, 12, 277
- [24] S.L. Lawton, R.A. Jacobson, Inorg. Chem. 1968, 7, 2124
- [25] S.L. Lawton, R.A. Jacobson, R.S. Frye, Inorg. Chem, 1971, 10, 701
- [26] A.M. Ganose, C.N. Savory, D.O. Scanlon, Chem. Commun. 2017, 53, 20
- [27] L.A. Frolova, D.V. Anokhin, A.A. Piryazev, S.Y. Luchkin, N.N. Dremova, K.J. Stevenson, P.A. Troshin, J. Phys. Chem. Lett. 2017, 8, 67
- [28] F. Hao, C.C. Stoumpos, D.H. Cao, R.P.H. Chang, M.G. Kanatzidis, *Nature Photonics* 2014, 8, 489
- [29] M. Garcia, P. Palacios, E. Menendez-Proupin, A.L. Montero-Alejo, J.C. Conesa, P. Wahnon, Sci. Rep. 2018, 8, 2511
- [30] M. Wojtas, R. Jakubas, Z. Ciunik, W. Medycki, J. Solid State Chem. 2004, 177, 1575
- [31] B. Jaschinski, R. Blachnik, H. Reuter, Z. Anorg. Allg. Chem. 1999, 625, 667
- [32] M. Wojtas, G. Bator, R. Jakubas, J. Zaleski, J. Phys.: Condens. Matter 2003, 15, 5765
- [33] A.T. Chaviara, A.C. Tsipis, P.J. Cox, C.A. Bolos, *Eur. J. Inorg. Chem.* 2005, 3491
- [34] R.F.W. Bader, Chem. Rev. 1991, 91, 893
- [35] D.M. Ivanov, M.A. Kinzhalov, A.S. Novikov, I.V. Ananyev, A.A. Romanova, V.P. Boyarskiy, M. Haukka, V.Yu. Kukushkin, *Cryst. Growth Des.* 2017, **17**, 1353
- [36] A.S. Mikhredov, M.A. Kinzhalov, A.S. Novikov, V.P. Boyarskiy, I.A. Boyarskaya, D.V. Darin, G.L. Starova, V. Yu. Kukushkin, *J. Am. Chem.* Soc. 2016, **138**, 14129
- [37] K. Kolari, J. Sahamies, E. Kalenius, A.S. Novikov, V.Yu. Kukushkin, M. Haukka, *Solid State Sci.* 2016, **60**, 92
- [38] D.M. Ivanov, A.S. Novikov, I.V. Ananyev, Y.V. Kirina, V. Yu. Kukuskin, *Chem. Commun.* 2016, **52**, 5565

- [39] E.R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A.J Cohen, W. Yang, J. Am. Chem. Soc. 2010, 132, 6498
- [40] D.M. Ivanov, A.S. Novikov, G.L. Starova, M. Haukka, V.Yu. Kukushkin, *CrystEngComm* 2016, **18**, 5278
- [41] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Reshati, G. Terraneo, *Chem. Rev.* 2016, **116**, 2478
- [42] E. Espinosa, E. Molins, C. Lecomte, Chem. Phys. Lett. 1998, 285, 170
- [43] M.V. Vener, A.N. Egorova, A.V. Churakov, V.G. Tsirelson, J. Comput. Chem. 2012, 33, 2303
- [44] E. Espinosa, I. Alkorta, J. Elguero, E. Molins, J. Chem. Phys. 2002, 117, 5529-5542
- [45] E.D. Glendening, C.R. Landis, F. Weinhold, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 1
- [46] S.A. Adonin, M.N. Sokolov, V.P. Fedin, Coord. Chem. Rev. 2018, 367, 1
- [47] T.A. Glukhova, A.I. Poddelsky, V.I. Faerman, Russ. Chem. Bull. 2015, 64, 329
- [48] A.I. Poddelsky, Y.A. Kurskii, A.V. Piskunov, N.V. Somov, V.K. Cherkasov, G.A. Abakumov, *Appl. Organomet. Chem.* 2011, **25**, 180
- [49] G.A. Fisher, N.C. Norman, Adv. Inorg. Chem. 41, 233
- [50] S.A. Adonin, M.A. Bondarenko, P.A. Abramov, A.S. Novikov, P.E. Plyusnin, M.N. Sokolov, V.P. Fedin, *Chem. Eur. J.*, DOI: 10.1002/chem.201801338
- [51] G.-E. Wang, G. Xu, B.-W. Liu, M.-S. Wang, M.-S. Yao, G.-C. Guo, Angew. Chem. Int. Ed. 2016, 55, 514
- [52] W. Bi, N. Louvain, N. Mercier, J. Luc, B. Sahraoui, *CrystEngComm* 2007, **9**, 298

Photoconductive metal-polyhalide

hybrids: In presence of different cations, reactions of $[SbBr_6]^{3^{\circ}}$ and I_2 result in a family of polyiodidebromoantimonate networks. Coordination number of Sb, as well as geometry of assembling $\{Br_xI_y\}^{n^{\circ}}$ polyhalide units, varies, resulting in unprecedented structural types. Some of the compounds showed strong photoconductivity in thin films, suggesting multiple feasible applications in optoelectronics and solar energy conversion.



Dr. Sergey A. Adonin,* Ms. Liubov I. Udalova, Dr, Pavel A. Abramov, Dr. Alexander S. Novikov, Dr.Denis G. Samsonenko, Ms. Irina V. Yushina, Dr. Ilya V. Korolkov, Dr. Evgeniy Yu. Semitut, Dr. Tatiyana A. Derzhavskaya, Prof. Dr. Keith J. Stevenson, Prof. Dr. Pavel A. Troshin, Prof. Dr. Maxim N. Sokolov and Prof. Dr. Vladimir P. Fedin

Page No. – Page No.

A novel family of polyiodobromoantimonate(III) complexes: cation-driven self-assembly of photoconductive metal-polyhalide frameworks

10.1002/chem.201802100