Harnessing ICl Reduction Processes for Synthesis of Different BEDT-TTF-Based Molecular Conductors

Elena Laukhina,*,†,‡ **Vladislava Tkacheva,**‡ **Igor Chuev,**‡ **Roman Wojciechowski,**§
Jacek Ulanski,§ **Jose Vidal-Gancedo,**† **Jaume Veciana,**† **Vladimir Laukhin,**†,# **and**
Concepció Rovira*,†

Institut de Ciència de Materials de Barcelona (CSIC) Campus UAB E-08193 Bellaterra, Spain, Institute of Problems of Chemical Physics (RAS) MD 142432 Chernogolovka, Russia, Department of Molecular Physics, Faculty of Chemistry, Technical University of Lódz, ul. Zeromskiego 116, 90-924 Lódz, Poland, and Institució Catalana de Recerca i Estudis Avançats (ICREA)

Both calculations and experimental data, showing the possibility of formation of I_3^-, I_2Cl^-, and ICl_2^- anions through ICl reduction processes, are described in detail. The above processes were used successfully for the preparation of different molecular conductors based on trihalide anions and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). The reaction between ICl and BEDT-TTF occurring in a strong polar reaction media ($\epsilon \geq 34.8$ D) results in the formation of novel molecular conductors containing different sets of the I_3^-, I_2Cl^-, and ICl_2^- anions: β-(BEDT-TTF)$_2$[(I$_3$)$_{0.4}$(I$_2$Cl)$_{0.6}$], β'-(BEDT-TTF)$_2$[(I$_2$Cl)$_{0.2}$(ICl$_2$)$_{0.8}$], and β''-(BEDT-TTF)$_2$-[(I$_3$)$_{0.075}$(I$_2$Cl)$_{0.150}$(ICl$_2$)$_{0.775}$]. These molecular conductors reveal semiconducting (β'-phase) as well as metallic (β- and β''-phases) transport properties. It is also shown that in the reaction media with polarity less than 18.4 D only the I_3^- anion is incorporated in the BEDT-TTF-based molecular crystals. This fact is an unexpected outcome of our study.

Introduction

Conducting molecular crystals based on trihalide salts of bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are the subject of numerous investigations because of their unusual bulk physical properties, which are modified easily by external influences, for example, pressure, temperature, irradiation, and so forth.[1−4] All of these compounds have a layered structure. Radical cations and neutral molecules of BEDT-TTF form conducting organic layers alternating with those of trihalide anions. The BEDT-TTF layer arrangements are controlled finely by donor-anion interactions, which in turn depend on the type of trihalide anion.[4−10] That is why BEDT-TTF trihalide salts have a different packing of the BEDT-TTF conducting layers. Eight general types of BEDT-TTF conducting layers have been reported in accordance with the BEDT-TTF packing pattern: β-, β'-, β''-, α-, α'-, α'''-, κ-, and θ-type.[4] Because the electronic properties of the salts are determined by the BEDT-TTF arrangement,[11,12] different BEDT-TTF layers show various electrical properties. For example, the β-, β''-, κ-, and θ-phases are metals and superconductors,[5,8,13,14] the α-type shows a metal−insulator transition,[6] and the β', α', and α''' layers exhibit a semiconductor behavior.[7,9,10] Recently, we have shown that incorporation of polar I_2Br^- and $BrICl^-$ anions into the structure of the BEDT-TTF salt leads to an intriguing set of structural phase transitions accompanied by a drastic change of electrical and magnetic properties of the crystals.[10] This result encouraged us to prepare new BEDT-TTF salts with another polar trihalide

anion, I_2Cl^-. The strategy for the generation of this anion in the crystallization process of BEDT-TTF trihalide salts envisaged the use of ICl reduction processes because we have already shown the formation of I_2Br^- anions via IBr reduction.[15,16] Another reason that provokes our interest in studying the interaction of ICl with BEDT-TTF is that ICl can be applied for the fabrication of a conducting crystalline layer of BEDT-TTF trihalide salts at the surface of a polymeric film.[15,17] Such types of bilayer film materials allow one to overcome the known technological limitations of single crystals of organic conductors (e.g., low processability, quantity, etc).

Herein, we shall focus on the possibilities and restrictions of a new synthetic method, which proposes the use of ICl reduction processes for the preparation of new conducting BEDT-TTF based salts with polar I_2Cl^- anions. We report the results of calculations that show the potentiality of the formation of polar I_2Cl^- anions through the reduction processes of ICl. We also show experimental data that establish a link between the types of BEDT-TTF trihalide salts formed via the BEDT-TTF + ICl reaction and polarity of the reaction media. In addition, the characterization (ESR, EDX, and Raman) and transport properties of molecular conductors that pioneered in containing polar I_2Cl^- anions, β-(BEDT-TTF)$_2$[(I$_3$)$_{0.4}$(I$_2$Cl)$_{0.6}$], β'-(BEDT-TTF)$_2$-[(I$_2$Cl)$_{0.2}$(ICl$_2$)$_{0.8}$], and β''-(BEDT-TTF)$_2$[(I$_3$)$_{0.075}$(I$_2$Cl)$_{0.150}$-(ICl$_2$)$_{0.775}$], are presented and discussed.

Experimental Section

Calculations. Ab initio calculations have been carried out on the MP2/LANL2DZ level (GAUSSIAN94).[18] The effect of the solvent was calculated according to the Onsager model.[19]

Preparation of Single Crystals by the BEDT-TTF + ICl Reaction. Under argon, at 120 °C, ICl (21 mg, 1.3×10^{-4} mol)

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* To whom correspondence should be addressed. E-mail: laukhina@icmab.es or cun@icmab.es.
† Institut de Ciència de Materials de Barcelona (CSIC).
‡ Institute of Problems of Chemical Physics (RAS).
§ Technical University of Lódz.
# ICREA.

TABLE 1: Data on the Synthesis of BEDT-TTF Trihalide Salts

solvent	solvent volume, mL	yield, %	crystal shape	crystal contribution, %	salt
NB	35	57	bars	<5	**1**
			needles	60−70	**2**
			plates	40−30	**3**
TCE(60%) + NB(40%)	35	15	bars	<40	**4**
			plates	>60	**5**
TCE	40	12	bars	<30	**6**
			plates	>70	**7**

TABLE 2: EDX Data for Two Different Crystals of Salts 1−7

salt	I, atomic %	Cl, atomic %	anion composition
1	79.3	20.7	$I_{2.4\pm0.1}Cl_{0.6\pm0.1}$
	81.6	18.4	
2	39.1	60.9	$I_{1.2\pm0.1}Cl_{1.8\pm0.1}$
	41.0	59.0	
3	43.3	56.7	$I_{1.3\pm0.1}Cl_{1.7\pm0.1}$
	41.4	58.6	
4	100		I_3
	100		
5	100		I_3
	100		
6	100		I_3
	100		
7	100		I_3
	100		

was added to a solution of BEDT-TTF (100 mg, 2.6×10^{-4} mol) in different organic solvents (see Table 1). The mixture of reagents was cooled to 25 °C with a rate of 1 C/h. As a result, black shining crystals with different shapes were obtained. The crystals were filtered and rinsed with ether; traces of the solvent were removed under vacuum. The total yield of the crystals was 12−57%.

Characterization of Crystals. Energy Dispersion X-ray spectroscopy (EDX) analysis was performed by a scanning electron microscope (SEM) HITACHI S-3000N with an EDX-NORAN instrument. The EDX data for all of the salts obtained (**1−7**) are summarized in Table 2. The well-known (BEDT-TTF)$_2$ICl$_2$ and (BEDT-TTF)$_2$I$_3$ molecular crystals were used as standards for calibration.

The Raman spectra were performed at 293 K at ambient pressure using a Jobin-Yvon T64000 Raman microscope spectrometer working in backscattering mode. The measurements were performed using the 632-nm laser line with 2 cm^{-1} resolution. The laser beam power was kept below 0.1 mW with an illuminated spot of about 8 μm in diameter, giving an energy density of 400 kW/m^2; diamond (1332 cm^{-1}) and silicon (520 cm^{-1}) were used for the calibration of the spectrometer. The Raman spectra of the crystals were taken at the (00l) crystallographic plane, and the incident electric field was polarized approximately along the long axis of the trihalide anions.

ESR spectra were recorded using a Bruker ESP-300E spectrometer operating in the X-band (9 GHz) with a rectangular TE$_{102}$ cavity and equipped with a field-frequency (F/F) lock accessory and a built-in Bruker NMR gaussmeter ER 035M. Rotations were performed by means of a Bruker programmable goniometer ER 218 PGl. Precautions to avoid undesirable spectral line broadening such as that arising from microwave power saturation and magnetic field overmodulation were taken.
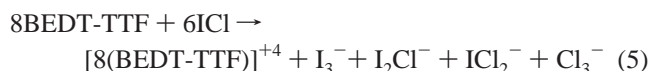
The temperature dependence of resistance of single crystals was measured using the standard four-probe dc method. Four annealed platinum wires (20 μm in diameter) were attached to the surface of the crystals by a graphite paste.

TABLE 3: Boltzman Probabilities (P) of the Proposed BEDT-TTF + ICl Reactions in TCE, TCE/NB Mixture, and NB

reaction	P_{TCE}	$P_{TCE/NB}$	P_{NB}
1	0.76	0.86	0.97
2	0.24	0.14	0.03
3	0	0	0
4	0	0	0
5	0	0	0

Results and Discussion

Thermodynamic Consideration of the BEDT-TTF + ICl Reaction. We assumed that the interaction of ICl with BEDT-TTF is a steady chemical reaction. This assumption allows us to estimate the probability (P) of each plausible BEDT-TTF + ICl reaction on the basis of Boltzman distribution $p \sim \exp(-E/RT)$, where E is energy of the reaction, R is the universal gas constant, and T is the temperature. The analysis of all of the possible results of the BEDT-TTF + ICl reaction producing species such as $I^{\pm1,0}$, $I_2^{\pm1,0}$, $I_3^{\pm1,0}$, $ICl^{\pm1,0}$, $Cl^{\pm1,0}$, $Cl_2^{\pm1,0}$, $Cl_3^{\pm1,0}$, $ICl_2^{\pm1,0}$, and $I_2Cl^{\pm1,0}$ restricts the set of the most energetically favorable reactions, which result in the maximum (2-fold) enhancement of the number of new bonds, by a factor of 5

$$8\text{BEDT-TTF} + 6\text{ICl} \rightarrow$$
$$[8(\text{BEDT-TTF})]^{+4} + 2I_2Cl^- + 2ICl_2^- \quad (1)$$

$$8\text{BEDT-TTF} + 6\text{ICl} \rightarrow$$
$$[8(\text{BEDT-TTF})]^{+4} + I_3^- + 3ICl_2^- \quad (2)$$

$$8\text{BEDT-TTF} + 6\text{ICl} \rightarrow$$
$$[8(\text{BEDT-TTF})]^{+4} + Cl_3^- + 3I_2Cl^- \quad (3)$$

$$8\text{BEDT-TTF} + 6\text{ICl} \rightarrow$$
$$[8(\text{BEDT-TTF})]^{+4} + 2I_3^- + 2Cl_3^- \quad (4)$$

$$8\text{BEDT-TTF} + 6\text{ICl} \rightarrow$$
$$[8(\text{BEDT-TTF})]^{+4} + I_3^- + I_2Cl^- + ICl_2^- + Cl_3^- \quad (5)$$

The energy of the reactions was calculated on the basis of an additive approach. This means that the intermolecular interactions of the reagents were not taken into consideration. For all of these reactions, we have compared only the energies of the species formed due to the reduction of ICl because the contributions of the other species are constant. On the basis of the calculations, the probability of reactions **3−5** equals zero (Table 3).

Thus, for the BEDT-TTF + ICl reaction, it would be plausible to suggest the formation of I_3^-, I_2Cl^-, and ICl_2^- trihalide anions only. We have estimated the contribution of each of these trihalide anions in different solvents that vary considerably in polarity (ϵ). We used nitrobenzene, NB, ($\epsilon = 34.82$ D) and trichloroethane, TCE, ($\epsilon = 7.55$ D) as strong and weak polar reaction media, respectively. We have also calculated the anion contribution for the NB(40%)−TCE(60%) mixture with polarity characterized by $\epsilon = 18.40$ D. These data are summarized in Table 4.

From the above calculation, the interaction of ICl with BEDT-TTF might result in the formation of anions favorable to different phases of BEDT-TTF trihalide salts: the largest I_3^- anion promoting the formation of α-, β-, κ-, and θ-phases,[4] whereas the smallest ICl_2^- is beneficial for the β′- or β″-one.[9,20] The conflict of crystallochemical interests between I_3^- and ICl_2^- species might provoke a formation of novel and/or known

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TABLE 4: Contribution (*C*) of Trihalide Anions Formed via the BEDT-TTF + ICl Reaction in TCE, TCE/NB Mixture, and NB

anion	C_{TCE}, %	$C_{TCE/NB}$, %	C_{NB}, %
I_3^-	6.5	3.4	0.75
I_2Cl^-	37.0	43.1	48.5
ICl_2^-	56.5	53.5	50.75

TABLE 5: Room-Temperature ESR Data for Salts 1−6

	parameters of the EPR signal				
	maximum		minimum		
salt	g	ΔH_{pp}, G	g	ΔH_{pp}, G	phase
1	2.0100	24	2.0028	20	β
2	2.0074	11	2.0029	8	β'
3	2.0110	53	2.0025	45	β''
4	2.0111	22	2.0027	18	β
5	2.0113	110	2.0025	70	α
6	2.0111	22	2.0027	18	β

different types of BEDT-TTF conducting layers. According to our calculations, the anion layer of single crystals obtained via the BEDT-TTF + ICl reaction might contain the following: (i) I_3^-, I_2Cl^-, or ICl_2^- as well as (ii) different combinations of these anions, such as (I_3^- and ICl_2^-), (I_2Cl^- and ICl_2^-), (I_3^- and I_2Cl^-), or (I_3^-, I_2Cl^-, and ICl_2^-). Moreover, the contributions of each trihalide anion can be different in crystals formed in various organic solvents.

Synthetic Aspects of Crystal Preparation. We have studied the preparation of BEDT-TTF trihalide salts via the BEDT-TTF + ICl reaction carried out in the above-mentioned organic solvents. Reaction conditions for the oxidation of BEDT-TTF by ICl were similar to those used for the preparation of high-quality crystals of β-(BEDT-TTF)$_2$I$_3$ organic superconductor via the BEDT-TTF + I$_2$ reaction.[21] Using NB as a solvent, we have obtained three different types of crystals: barlike (**1**), needlelike (**2**), and platelike (**3**) crystals (see Table 1). In TCE or in the mixture of TCE (60%) and NB (40%), the above method results in a surprisingly small scale production (yield 12−15%) of two different types of crystals: bars (**4**, **6**) and plates (**5**, **7**).

Phase Identification. A rich polymorphism of BEDT-TTF trihalide salts[2−4] must always be kept in mind when it comes to analyzing crystals formed through any crystallization process of BEDT-TTF trihalide salts. This analysis is difficult because of the fact that crystals of the same polymorphic modification can differ in shape and, conversely, crystals of the same shape can differ in phase.[2,3,21] In addition, different structural phase transitions occurring in these salts as a function of pressure or temperature hamper the use of a powder X-ray diffraction analysis: the phase composition of initial crystals may differ from that of the powder sample prepared for X-ray. To overcome the above problems related with the phase identification, we applied the ESR characterization method because the structural packing motif, or the surrounding symmetry of each BEDT-TTF radical cation in the crystal, mainly determines the value of the peak-to-peak line width (ΔH_{pp}).[2,3] Thus, it is clear that with a measurement of the ESR line width a fairly accurate phase identification can be made.

To identify the type of salts **1−7**, we studied the anisotropy of the room-temperature ESR signals for different crystals of each morphology and compared these ESR data, summarized in Table 5, with those for the known BEDT-TTF trihalide salts.[22−25] The analysis of ESR data allows us to identify crystals **1**, **4**, and **6** as β-phase, whereas crystals **2**, **3**, and **5** as β'-, β''-, and α-phase, respectively. The ESR signal of **7** is very broad and too weak to identify this compound unambiguously. The
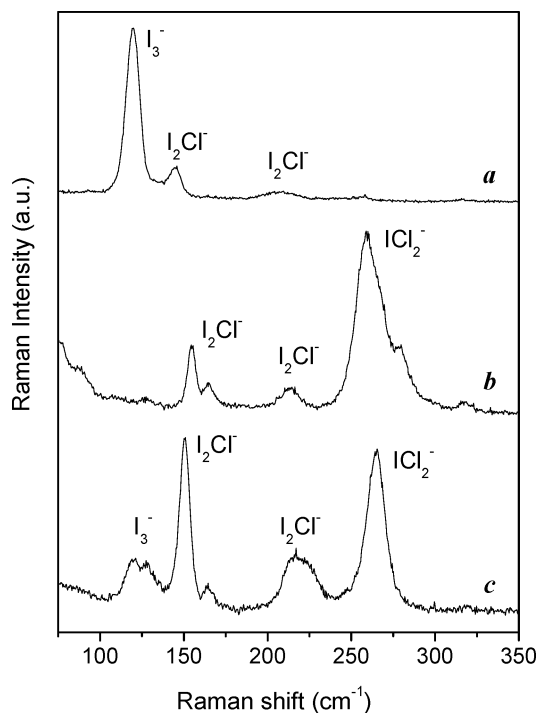
Figure 1. Room-temperature Raman spectra of (a) **1**, (b) **2**, and (c) **3**.

cell parameters of **7** (a = 16.40 Å, b = 8.50 Å, c = 12.80 Å, α = 90°, β = 108°, γ = 90°) determined from Weissenberg photographs correspond to k-(BEDT-TTF)$_2$I$_3$ phase[8] that correlates well with the broad ESR signal observed.[2,26] Taking into account that these structural phases were formed at a different polarity of the reaction media, salts **1−7** can also differ in composition. We have selected several crystals of the same ESR signal from each synthesis and study their compositions and electrical properties. This study shows that crystals of similar shape from each synthesis are identical in composition as well as uniform in phase.

Composition of 1−7. On the basis of the EDX data (see Table 2), **1**, **2**, and **3** were found to be (BEDT-TTF)$_2$I$_{2.4\pm0.1}$-Cl$_{0.6\pm0.1}$, (BEDT-TTF)$_2$I$_{1.2\pm0.1}$Cl$_{1.8\pm0.1}$, and (BEDT-TTF)$_2$I$_{1.3\pm0.1}$-Cl$_{1.7\pm0.1}$, respectively. It is clear that only a set of trihalide species can result in the anion composition like I$_x$Cl$_{3-x}$ (1 < x < 2 or 2 < x < 3). This result reveals good agreement with the thermodynamic analysis of the ICl reduction processes (see above). EDX data for salts **4−7** show a lack of Cl atoms. The atomic contribution of S and I in **4−7** is the same and is approximately 84% and 16%, respectively. These values correspond to the composition of the known (BEDT-TTF)$_2$I$_3$ salt in which the atomic percent of the above elements is 84.21% (S) and 15.79% (I). Besides EDX, Raman spectroscopy was used to answer the question of which trihalide anions play the principal role for the formation of **1−3**.

The Raman spectrum of the crystal of **1** (Figure 1a) shows bands at 120, 147, and 208 cm^{-1}. The band at 120 cm^{-1} originates from the Σ_g^+ mode of the symmetrical linear I$_3^-$ anions.[27,28] The band at 147 and the broad band at 208 cm^{-1} may be attributed to the Σ^+ modes of nonsymmetrical linear I$_2$Cl$^-$ anions.[29] The Σ_g^+ mode of the symmetrical linear ICl$_2^-$ anions is not observed in the spectrum. Unfortunately, the resonance effect well known for vibrations of the I$_3^-$ anion[28] makes an estimation of the contribution of the above anions based on the integrated band area impossible, but the absence of the band corresponding to the smallest ICl$_2^-$ anions allows us to estimate this contribution using EDX analysis. Based on
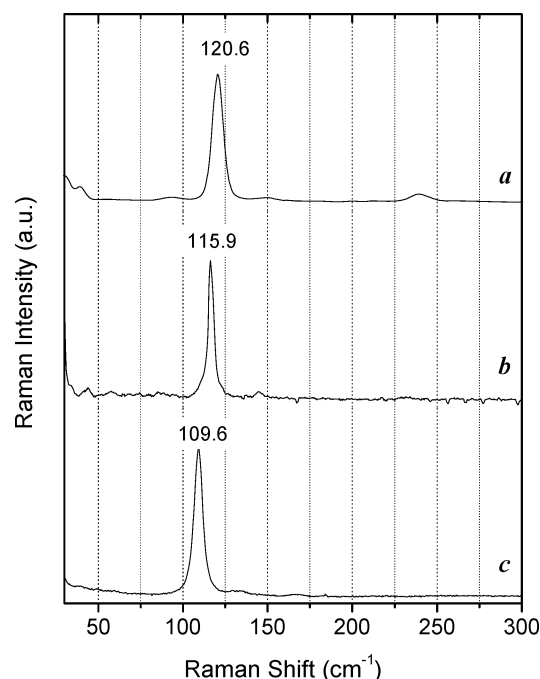
Figure 2. Room-temperature Raman spectra of (a) **4** or **6**, (b) **5**, and (c) **7**.

the EDX data, the most possible composition of **1** is (BEDT-TTF)$_2$(I$_3$)$_{0.4}$(I$_2$Cl)$_{0.6}$.

The spectrum of **2** (Figure 1b) shows one very intensive band at 259 cm^{-1} that corresponds to the in-phase stretch vibrations of ICl$_2^-$ anions[28] and two bands of less intensity at 155 cm^{-1} and at 213 cm^{-1}, which are characteristic of I$_2$Cl$^-$ anions.[29] The Σ_g^+ mode of I$_3^-$ anions is not observed in this spectrum. Therefore, taking into account EDX data, the plausible composition of **2** can be presented as (BEDT-TTF)$_2$(I$_2$Cl)$_{0.2}$(ICl$_2$)$_{0.8}$.

In the spectrum of **3** (Figure 1c), one can find bands at 121, 150, 265, and a broad band at 218 cm^{-1}. The bands at 121 and 265 cm^{-1} are induced by the Σ_g^+ mode of I$_3^-$ and ICl$_2^-$ anions, respectively.[27−29] The moderate intensity of the 121 cm^{-1} band, which is usually enhanced by resonant condition, suggests that the admixture of I$_3^-$ anions is very small. The band at 150 and the broad band at 218 cm^{-1}, like the 147 and 208 cm^{-1} ones in the spectrum of **1**, may be attributed to the Σ^+ modes of nonsymmetrical linear I$_2$Cl$^-$ anions. Taking into account both Raman and EDX data, it is possible to estimate the plausible proportion of trihalide anions in **3**. Their contributions might vary from [(I$_3$)$_{0.05}$(I$_2$Cl)$_{0.2}$(ICl$_2$)$_{0.75}$]$^-$ to [(I$_3$)$_{0.1}$(I$_2$Cl)$_{0.1}$(ICl$_2$)$_{0.8}$]$^-$. Therefore, the most credible composition of **3** is of (BEDT-TTF)$_2$(I$_3$)$_{0.075}$(I$_2$Cl)$_{0.150}$(ICl$_2$)$_{0.775}$.

The Raman spectra of **4−7** (Figure 2) show only one intensive band that corresponds to the in-phase stretch vibrations of I$_3^-$ anions[27,28] in agreement with the halogens' contribution revealed by EDX (see Table 2). Therefore, we may identify crystals **4−7** as the well-known (BEDT-TTF)$_2$I$_3$ salt.

It must be emphasized that the position of the Raman band of I$_3^-$ anions is consistent with the structure of the BEDT-TTF layer in (BEDT-TTF)$_2$I$_3$ polymorphs.[27,28] Therefore, we can use Raman spectra to get additional information on the phase of trihalide salts **1** and **4−6** (where the I$_3^-$ peak is dominant). Because the band at 120 cm^{-1} is observed for the β phase of (BEDT-TTF)$_2$I$_3$, we may identify **4** and **6** as β-(BEDT-TTF)$_2$I$_3$. In the Raman spectrum of **1**, the I$_3^-$ band is also observed at 120 cm^{-1}, showing that this phase contains the β-BEDT-TTF layer as well. The spectrum of **5** shows the band of I$_3^-$ at 115.9 cm^{-1} that is characteristic to the α-polymorph of (BEDT-TTF)$_2$I$_3$.[27] These results are in good agreement with the above ESR data. In the spectrum of **7**, this band is shifted to 109.6 cm^{-1} suggesting that the BEDT-TTF packing of **7** differs from that of **4−6**. Taking into account both X-ray and EDX data, we may assign this band to the Σ_g^+ mode of the symmetrical linear I$_3^-$ anions in κ-(BEDT-TTF)$_2$I$_3$.

Keeping in mind the complexity of the Raman spectra for new molecular conductors **2** and **3**, we have confirmed the phase identification based on the ESR spectra, by studying their Weissenberg photographs. The cell parameters of **2** ($a = 6.60$ Å, $b = 9.80$ Å, $c = 12.93$ Å, $\alpha = 87°$, $\beta = 79°$, $\gamma = 82°$) and **3** ($a = 5.80$ Å, $b = 9.00$ Å, $c = 16.30$ Å, $\alpha = 83°$, $\beta = 96°$, $\gamma = 104°$) correspond to β' and β'' phase, respectively,[7,24] that correlates well with the observed ESR signals.
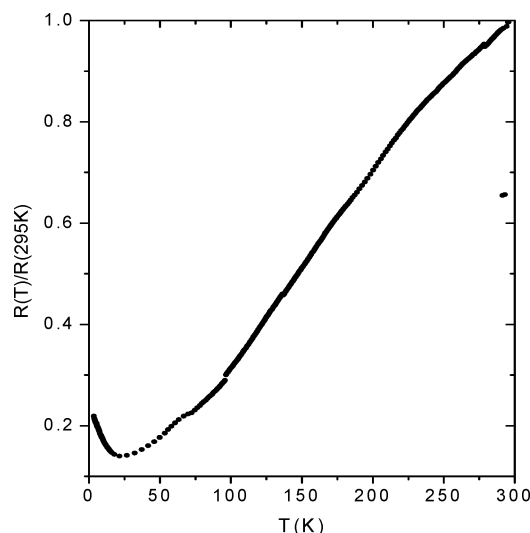
The Role of I$_3^-$ in the Crystallization of BEDT-TTF Trihalide Salts. The data summarized in Table 6 show the relationship between the contributions of trihalide anions generated by ICl reduction processes performed at different polarity of the reaction media and the phase composition of the crystallized BEDT-TTF trihalide salts.

From these data, one may conclude that the amount of I$_3^-$ in the collection of trihalide anions, which is introduced by the BEDT-TTF + ICl reaction, is of crucial importance. Even at low concentrations (3−6%) of I$_3^-$ anions, only the crystals of the most thermodynamically stable (BEDT-TTF)$_2$I$_3$ salt are formed. However, when the polarity of the reaction media results in the formation of the largest I$_3^-$ anions in very low concentrations (<1%), the molecular crystals of novel BEDT-TTF based salts containing different sets of trihalide anions are generated. These new BEDT-TTF salts contain polar I$_2$Cl$^-$ anions, which together with I$_3^-$ and/or ICl$_2^-$ play an important role in formation of metallic β-, β''- or semiconductor β'-BEDT-TTF layers. Crystallization of BEDT-TTF-based salts in the presence of different trihalide anions is a very complicated process, which is governed by different factors: diffusion, crystallochemistry laws, interaction between solvent and crystal building blocks, and so forth. This makes it difficult to answer the question of why I$_2$Cl$^-$ and ICl$_2^-$ anions are not involved in the crystallization of BEDT-TTF-based conductors with the TCE present. Possibly, the concentration of I$_3^-$ anions in TCE is enough to provoke the crystallization of (BEDT-TTF)$_2$I$_3$ crystals. This reduces the concentration of the donor in the solvent as well as

TABLE 6: Characteristics of the Reaction Media (Solvent, Polarity (ϵ), Anions' Contribution) and the Type of BEDT-TTF Trihalide Salts Formed via the BEDT-TTF + ICl Reaction

		anions' contribution (%)			
solvent	ϵ, D	I$_3^-$	I$_2$Cl$^-$	ICl$_2^-$	type and composition of the salt
NB	34.82	0.75	48.5	50.75	β-(BEDT-TTF)$_2$ [(I$_3$)$_{0.4}$(I$_2$Cl)$_{0.6}$] (**1**)
					β'-(BEDT-TTF)$_2$[(I$_2$Cl)$_{0.2}$(ICl$_2$)$_{0.8}$] (**2**)
					β''-(BEDT-TTF)$_2$[(I$_3$)$_{0.075}$(I$_2$Cl)$_{0.150}$(ICl$_2$)$_{0.775}$] (**3**)
TCE (60%) +NB (40%)	18.40	3.4	43.1	53.5	β-(BEDT-TTF)$_2$I$_3$ (**4**)
					α-(BEDT-TTF)$_2$I$_3$ (**5**)
TCE	7.55	6.5	37.0	56.5	β-(BEDT-TTF)$_2$I$_3$ (**6**)
					κ-(BEDT-TTF)$_2$I$_3$ (**7**)

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Figure 3. Temperature dependence of normalized resistance for the β-(BEDT-TTF)$_2$[(I$_3$)$_{0.4}$(I$_2$Cl)$_{0.6}$] crystal (**1**).

the probability of reaction **1**, and, consequently, crystals of more soluble (BEDT-TTF)$_2$(I$_2$Cl)$_x$(ICl$_2$)$_y$ salts are not able to be formed. Thus, even a very small amount of I$_3^-$ anions, which can be generated at some conditions of preparation of new BEDT-TTF-based salts, might provoke crystallization of the well-known polymorphs of (BEDT-TTF)$_2$I$_3$ salt, reducing the probability of formation of novel organic conductors to zero.

Electrical Properties of New BEDT-TTF Trihalide Salts Containing Polar I$_2$Cl$^-$ Anions. In what follows, we will consider how the structural adjustment of the β-, β'-, and β''-BEDT-TTF conducting layers by the mixtures of the trihalide anions relates to the transport properties of **1**–**3**.

The room-temperature conductivity of **1** (β-phase) measured parallel to the layers is 10–50 Scm^{-1}. This value is the same as the one reported for the β-(BEDT-TTF)$_2$I$_3$ crystal ($\sigma_{//} = 20$–50 Scm^{-1}).[5] The temperature dependence of the resistance of **1** is metal-like within the temperature range 20–293 K (Figure 3). But, in contrast to the isostructural β-(BEDT-TTF)$_2$X (X = I$_3^-$, IBr$_2^-$, and AuI$_2^-$) superconductors, the new β-(BEDT-TTF)$_2$[(I$_3$)$_{0.4}$(I$_2$Cl)$_{0.6}$] salt does not reveal a superconductor transition. Below 20 K, the resistance increases slightly, most probably resulting from the localization of carriers, which can be caused at low temperature by the disorder in the anion layer as it was observed for the β-(BEDT-TTF)$_2$[(I$_3$)$_{0.07}$(I$_2$Br)$_{0.37}$-(IBr$_2$)$_{0.56}$] molecular crystals.[16] The overall decrease of the resistance R_{295}/R_{20} is ~7.

The room-temperature conductivity of **2** (β'-phase), when the current is running parallel to the layers was measured to be ($\sigma_{//}$) $\approx 2 \times 10^{-2}$ Scm^{-1} and the $R(T)$ shows a semiconductor-like behavior. The activation energy value was found to be 76 meV. This value is lower than that reported for the β'-(BEDT-TTF)$_2$ICl$_2$ crystal,[20] but it is very close to that found for another β'-(BEDT-TTF)$_2$[(IBr$_2$)$_{0.2}$(BrICl)$_{0.1}$(ICl$_2$)$_{0.7}$] crystal.[24]

In the plane parallel to the layers of **3** (β''-phase) the room-temperature conductivity is 70–100 Scm^{-1}. This value is lower than that reported for the β''-(BEDT-TTF)$_2$ICl$_2$ crystal ($\sigma_{//}$ = 200 Scm^{-1}).[20] The temperature dependence of the resistance of **3** is metal-like within the temperature range 13–293 K (Figure 4). Below 13 K, the resistance increases slightly, as was observed for the isostructural β''-(BEDT-TTF)$_2$[(IBr$_2$)$_{0.2}$-(BrICl)$_{0.1}$(ICl$_2$)$_{0.7}$] crystal.[24] Similar to the β''-(BEDT-TTF)$_2$ [(IBr$_2$)$_{0.2}$(BrICl)$_{0.1}$(ICl$_2$)$_{0.7}$] salt,[24] the low-temperature increase of the resistance of **3** might result from the localization of carriers due to disorder in its structure caused by the mixture
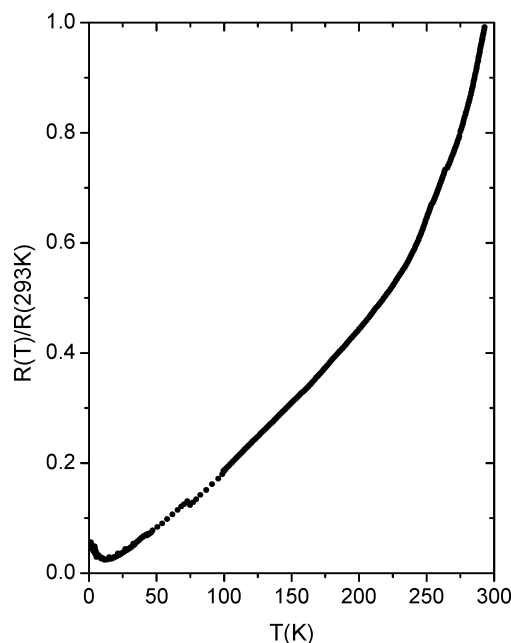
Figure 4. Temperature dependence of normalized resistance for the crystal of the β''-(BEDT-TTF)$_2$[((I$_3$)$_{0.075}$ I$_2$Cl)$_{0.150}$(ICl$_2$)$_{0.775}$] salt (**3**).

of anions. The overall decrease of the resistance R_{293}/R_{13} was found to be ~40.

The resistance measurements show that the structural adjustment of the β-, β'-, and β''-BEDT-TTF conducting layers by the mixture of the trihalide anions incorporated in salts **1**–**3** determines their transport properties similar to the structural adjustment of the β-, β'-, and β''-BEDT-TTF conducting layers in the β-(BEDT-TTF)$_2$[(I$_3$)$_{0.07}$(I$_2$Br)$_{0.37}$(IBr$_2$)$_{0.56}$], β'-(BEDT-TTF)$_2$[(IBr$_2$)$_{0.2}$(BrICl)$_{0.1}$(ICl$_2$)$_{0.7}$], and β''-(BEDT-TTF)$_2$[(IBr$_2$)$_{0.2}$-(BrICl)$_{0.1}$ (ICl$_2$)$_{0.7}$] salts.[16,24]

Summary

The main goal of this study is to show that ICl reduction processes result in the formation of three types of trihalide anions: I$_3^-$, I$_2$Cl$^-$, and ICl$_2^-$, the contributions of each anion depending on the polarity of the reaction media.

It was demonstrated that ICl reduction processes performed in a polar environment can be applied for the preparation of new conducting BEDT-TTF based salts containing polar non-symmetrical I$_2$Cl$^-$ anions. These anions in combination with the larger I$_3^-$ ones can be integrated successfully in the architecture of molecular crystals with metallic β-BEDT-TTF layers, whereas together with the smaller ICl$_2^-$ anions they result in the formation of either semiconducting β'- or metallic β''-BEDT-TTF layers.

The relationship between the contribution of the trihalide anions formed via the BEDT-TTF + ICl reaction and the types of the crystallized BEDT-TTF salts reveals that the amount of I$_3^-$ is of crucial importance: even a very small quantity of I$_3^-$ might reduce the probability of formation of the BEDT-TTF based salt, which is different from the well-known (BEDT-TTF)$_2$I$_3$ one, to zero.

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