

Electrocrystallization, an Invaluable Tool for the Construction of Ordered, Electroactive Molecular Solids[†]

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For the past three decades, the electrocrystallization technique has been used extensively to assemble a large variety of molecular ions into long range ordered single crystals of high purity. This effort is reviewed in the present paper from the initial vigorous impetus triggered by the development of organic (molecular) metals and superconductors to the continuous diverse developments toward insulating antiferromagnetic systems, the synthesis of crystals of coordination polymers, the construction of ternary and quaternary phases, the variation of molecular conformation, the use of polyfunctionalized π -donor molecules with hydrogen-bond-donor and/or -acceptor capabilities and the development of molecular alloys, with the aim of exemplifying an approach to the solid-state chemistry of molecular ions.

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Introduction

The construction of ordered molecular assemblies by electrochemical association of organic cation radical molecules with large, eventually redox-active, inorganic anions lies at the heart of our approach toward the solid-state chemistry of molecular ions.¹ The relative orientation and site location of the large and complex polyfunctionalized molecular units—be they organic,² metallo-organic or mineral (all inorganic)—results from intermolecular interactions (for example, van der Waals bonding vs H-bonding vs π - π interactions) that can be balanced by using appropriate fragments or ligands in order to modify and even control the structure of the solids and their functions. The purpose of this paper is to review the salient features and underline the potential of the electrocrystallization technique, a versatile, invaluable tool to assemble molecular ions into high-quality single crystals (Figure 1).

The first electrolysis experiment reported to yield a crystalline molecular solid was described in 1971.³ The galvanostatic oxidation of arenes such as perylene, pyrene, or azulene in THF solutions containing *n*-Bu₄NClO₄ as the electrolyte afforded black single crystals on the anode, shown by elemental analysis and X-ray

structure determination to be the 2:1 salts (Ar)₂ClO₄, i.e., a mixed-valence salt with a partial charge transfer ρ (where $\rho = 0.5$). Chiang noted at that time that the crystals were conducting and thus continue to grow on the electrode. This was the basis for further developments of the technique. In 1973, the discovery of metallic conductivity⁴ in TTF·TCNQ, a charge-transfer salt obtained from the chemical redox reaction of tetrathiafulvalene (TTF) “an electron-rich olefin”,^{5,6} with the electron acceptor tetracyanoquinodimethane, TCNQ,⁷ gave a new impetus to the field of organic conductors, and a wealth of new tetrathiafulvalene-based donor molecules were synthesized.⁸ These molecules were engaged with acceptor molecules such as TCNQ or TCNQF₄ in order to investigate the effects of chemical and structural modifications of the prototypical system TTF·TCNQ.^{9,10} TTF itself was galvanostatically electrocrystallized with a variety of small anions ($X^- = \text{NO}_3^-, \text{Br}^-, \text{HCO}_3^-, \text{BF}_4^-$) yielding mixed-valence salts TTFX_{*n*}.¹¹ In the latter seminal contribution and the accompanying paper prepared for the Boulder International Conference on Low-Dimensional Conductors,¹² Rosseinsky et al. not only reported that the electroreduction of TCNQ affords electrocrystallized materials but also offered a set of empirical observations, such as the description of current–time behavior during potentiostatic crystal growth, which inspired the practitioners in the field of organic metals for many years to come.

In 1979, the observation that the metallic character of the segregated stack charge-transfer complex TMTSF·DMTCNQ remains mainly attributable to the TMTSF stack at low temperatures¹³ led Klaus Bechgaard to prepare mixed-valence salts of TMTSF with closed-shell anions such as PF₆⁻ or ClO₄⁻, paralleling the electrocrystallization of the all-sulfur analogue TMTTF reported by Fabre et al.¹⁴ Electrocrystallization of TMTSF in the presence of *n*-Bu₄NPF₆ or *n*-Bu₄NClO₄ afforded centimeter-long crystals of the Bechgaard salts, the

[†] Dedicated to the memory of Jean Rouxel

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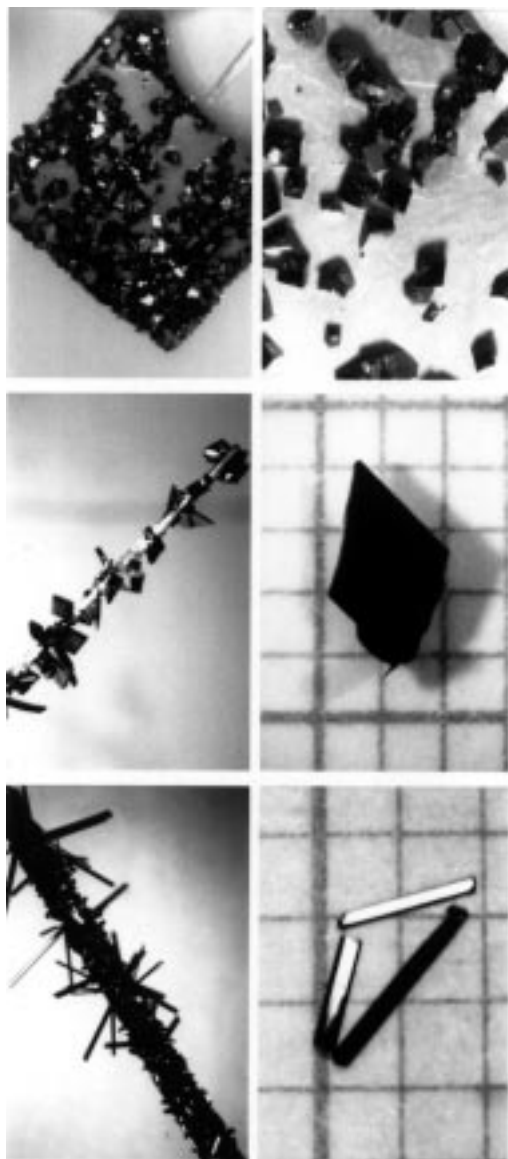


Figure 1. Examples of single crystals grown by electrocrystallization, from bottom to top: (i) needlelike crystals of the 1D conducting system $(\text{TMTSF})_5(\text{Nb}_6\text{Cl}_{18})(\text{CH}_2\text{Cl}_2)_{0.5}$;⁴² (ii) plates, growing perpendicular to the electrode, of the 2D metallic salt $\beta\text{-(BEDT-TTF)}_4(\text{Re}_6\text{S}_6\text{Cl}_8)\cdot(\text{dioxane})$;⁵⁴ (iii) rhombohedral crystals of the antiferromagnetic, molecular antiperovskite $(\text{TTF}^+)_3(\text{Mo}_6\text{Cl}_{14}^{2-})(\text{Cl}^-)$.⁹⁸

prototypical $(\text{TMTSF})_2\text{X}$ series (Figure 2) of single-chain one-dimensional organic metals and superconductors. The observation of superconductivity ($T_c = 0.9$ K) in $(\text{TMTSF})_2\text{PF}_6$ at 12 kbar and then in $(\text{TMTSF})_2\text{ClO}_4$ ($T_c = 1.2$ K) at ambient pressure^{15,16} allowed a rich low dimensional physics to be unraveled, where comparatively weak interactions between the molecular cation radicals in the solid-state translate into collective low-energy excitations, giving rise to an electronic state called a Luttinger liquid, a matter of continuous intense interest.¹⁷ These wide-ranging developments certainly qualify the electrocrystallization method as an invaluable tool¹⁸ for the synthesis of conducting or superconducting materials of very high purity. In some instances, the limited thermodynamic stability of the electrogenerated cation radicals or their poor solubility prevents other methods from being used. Therefore, electrocrystallization appears to be a general synthetic

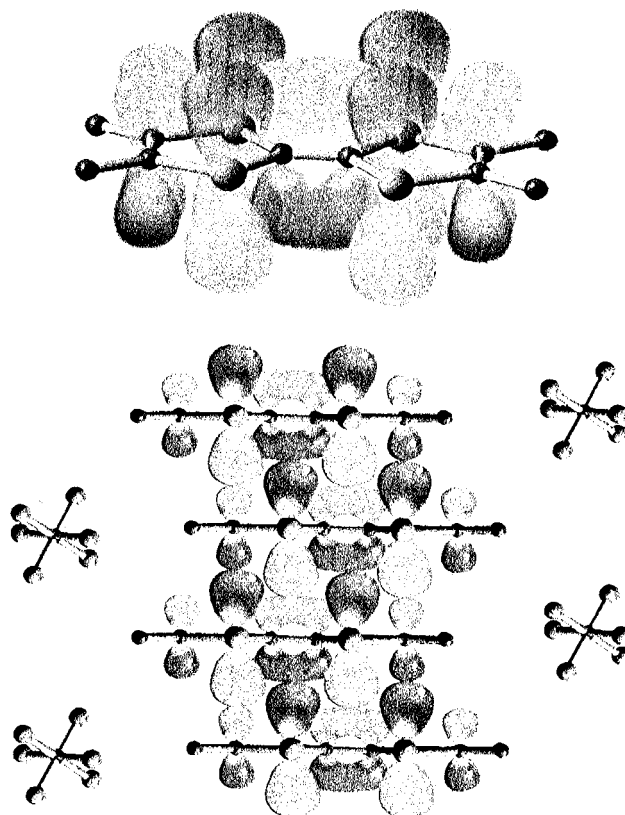


Figure 2. (upper) the HOMO symmetry of tetramethyltetraselenafulvalene, TMTSF; (lower) a view of the overlap pattern of the donor stack HOMOs and the anion cavities in the Bechgaard salt, $(\text{TMTSF})_2\text{PF}_6$, synthesized by electrocrystallization.

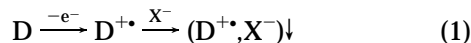
method for generating and assembling charged or neutral open-shell molecules; its implementation is easily carried out and its potential in solid-state supramolecular chemistry appears unlimited, not only for conducting and insulating systems, as emphasized in this paper, but also for charge-transfer complexes.¹⁹

It should be noted that there exists abundant literature on the related topic—outside the scope of the present review—of electrodeposition and electrocrystallization of metals with important applications in metallurgy and interfacial electrochemistry.²⁰

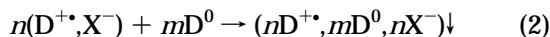
Electrocrystallization: Principles

The method requires an electroactive species, neutral or charged, whose electro-oxidation (or reduction) leads to a stable radical. If soluble, the generated radical species may diffuse into solution, but under suitable conditions of concentration, solvent, temperature, and current density, they will precipitate (crystallize) on the electrode, sometimes associated with neutral molecules and/or counteranions. The use of a stable and constant direct current source allows the number of electrons delivered to the electrode to be fine-tuned, thus controlling the local concentration of electroactive species and, hence, the rate of crystal growth. The three other parameters, namely concentration, solvent,²¹ and temperature, essentially control the solubility of the crystalline phase. The appropriate combination of these factors, together with the use of high-purity starting materials, ultimately determines the success of the electrocrystallization experiment.

Consider the most common reaction, i.e., oxidation of a neutral donor molecule. The salt generated at the electrode may crystallize with a 1:1 stoichiometry (eq 1)



Frequently however, and particularly when using planar conjugated organic molecules with π electrons, the radical cation formed at the electrode associates with one or more neutral donor molecules (most probably in solution before crystallization occurs), producing materials with other stoichiometries, for example, 1:2 or 2:3 (eq 2):



In this latter case, the electrocrystallization process is highly favored as such mixed valence salts are often good conductors and therefore also function as an electrode and hence the crystals may grow upon themselves. However, an early mechanistic observation by Rosseinski et al. reported that, in the case of TTFI_{0.71}, crystals poked out through the liquid surface, suggesting that the actual crystal growth was occurring at the Pt surface rather than at the distant crystal end.¹² Clearly, such mechanistic aspects, very much correlated to the actual geometry of the electrocrystallization cell,^{20a,b} require further studies in interfacial molecular electrochemistry.

An interesting question that remains to be settled is, where does the $(D^{+\bullet}/nD^0)$ association take place, i.e., in solution, at the surface of the crystal, or solely at the electrode/crystal interface? For arene molecules such as fluoranthene or naphthalene, ESR studies in solution²² and electrochemical measurements²³ have clearly shown that dimers $(D_2)^{+\bullet}$ are formed in solution preceding the crystallization step. Furthermore, it appears that such associations/aggregates are precursors of the final crystal formulation and may be controlled, in particular, by adjusting the charge of the counterion in solution. Indeed, we recently demonstrated that substitution of the dianionic $Re_6S_6Cl_8^{2-}$ for the mono-anionic, isosteric $Re_6S_5Cl_9^{1-}$ in electrocrystallization experiments with a tetrathiafulvalene derivative containing two TTF moieties covalently linked through an ethylenic bridge, $Me_2TTF-CH_2-CH_2-TTFMe_2$, led respectively to intermolecular associations of the donor into triads (with $Re_6S_6Cl_8^{2-}$) and diads (with $Re_6S_5Cl_9^{1-}$),²⁴ a clear-cut example of the effect of the charge of the inorganic template.

Electrocrystallization: the Experiment

A drawing of a typical electrocrystallization cell is given in Figure 3. A platinum wire²⁵ is used as the working electrode. It has also been shown that the presynthesis treatments of the electrode, such as polishing with fine sand paper and electrolysis in 1 M H_2SO_4 solution, can lead to different crystalline phases (polymorphism).²⁶ The choice of the electrolysis solvent is limited by its ability to dissolve both the organic donor and the electrolyte.²¹ For this purpose, a mixture of two or more solvents may be required, but one must keep in mind that ultimately the salt of the electro-oxidized

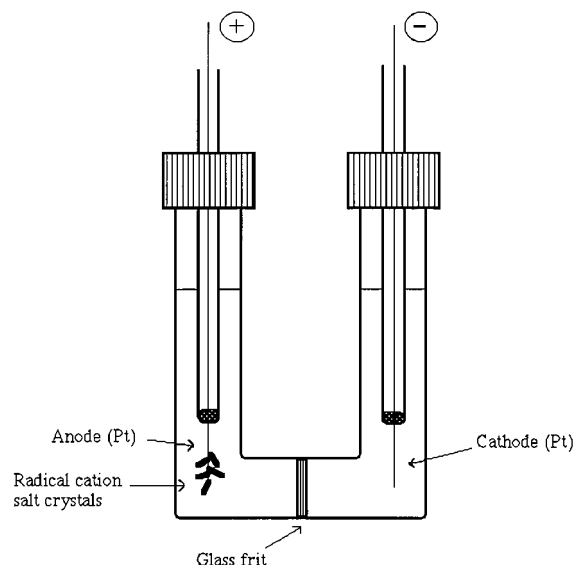


Figure 3. An electrocrystallization cell used in our laboratory.

species must not be soluble if it is to crystallize. The electrocrystallization cell volumes typically used in our laboratory range from 10 mL, which allow a few milligrams of crystals to be obtained, to several liters when gram quantities are needed.

Electrocrystallization allows high-purity materials to be reproducibly obtained only if all materials and chemicals involved are properly purified. This includes the glassware, which should be thoroughly cleaned; however sulfochromic mixture should be avoided because of its toxicity and also to avoid the introduction of paramagnetic impurities into the final product. In our laboratory, the electrodes are cleaned by electrolysis in 1 M H_2SO_4 solutions, by alternating the direction of current, and then rinsed with water prior to drying. Solvents of high-purity grade are dried on activated alumina or are distilled just prior to use. Finally, the electrolyte, as well as the donors, are recrystallized three times, and the latter are ultimately purified by sublimation whenever possible.²⁷ In addition to those recrystallization and sublimation procedures, the preparation of the organic donor molecule has been demonstrated to also play a role. For example, the superconducting transition temperature ($T_c = 10.4$ K) of κ -(BEDT-TTF)₂Cu(NCS)₂ (Figure 4) is unanimously and repeatedly observed^{28,29} to be highest when BEDT-TTF is synthesized using the Larsen–Lenoir synthesis.³⁰

Electrocrystallization is most often carried out in the galvanostatic mode using a current on the order of 1 μA for a platinum electrode 1 mm in diameter and approximately 2 cm long. These values can be increased or decreased by 1 order of magnitude, depending upon the solubility of the final salt. A few examples of potentiostatic electrocrystallization have been reported,¹² thus allowing the oxidation state, and hence the stoichiometry of the product, to be controlled, as demonstrated with lithium phthalocyanine,³¹ hexamethoxytriphenylene,³² and 1:1 salts of BEDT-TTF.³³

Electrocrystallization: A Wide Variety of Partners

The Electrolyte. The electrolyte is typically introduced as a tetraalkylammonium or tetraphenylphos-

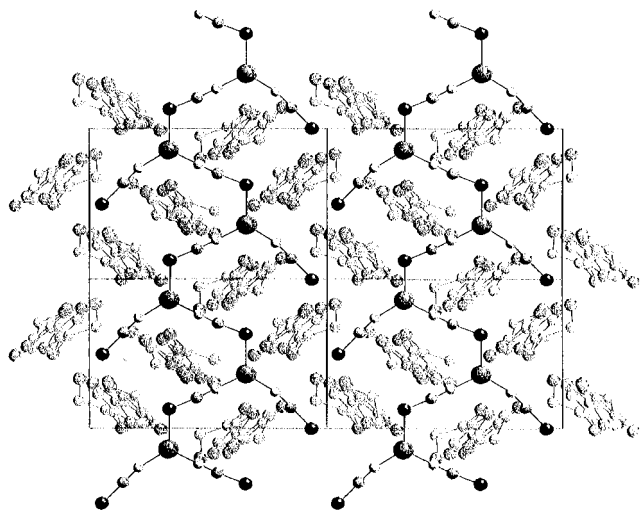


Figure 4. The polymeric anionic network which develops during the electrocrystallization of the 2D organic metal and superconductor κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ and projected onto a single organic slab, paved with orthogonal, interacting, mixed-valence BEDT-TTF dimers.

phonium salt to ensure its solubility in the organic solvents necessary to dissolve the donor molecules. The electrolyte counteranion needs to be stable at the working oxidation potential. Most superconducting organic cation radical salts are based on TMTSF³⁴ or BEDT-TTF³⁵ associated with small, closed-shell anions which can be classified according to their geometry: monatomic, e.g., Cl⁻, Br⁻ (fluoride salts are still unknown); planar anions, e.g., NO₃⁻; tetrahedral anions, e.g., ClO₄⁻, ReO₄⁻, FeCl₄⁻, GaCl₄⁻; octahedral anions, e.g., ReCl₆²⁻,³⁶ PF₆⁻, AsF₆⁻, SbF₆⁻; linear anions, e.g., I₃⁻, HCl₂⁻,³⁷ AuI₂⁻, Ag(CN)₂⁻; square planar anions, e.g., AuX₄⁻ (X = Cl, Br, CN),^{38,39} Cu(CF₃)₄⁻;⁴⁰ two-dimensional polymeric anions, e.g., Cu(NCS)₂⁻, Cu[N(CN)₂]Br⁻, KHg(SCN)₄⁻.

In addition to these now classical examples, more complex anions with a wide variety of shapes, charges, electronic structures, and redox and magnetic states can be used (Figure 5). For example, magnetic anions, such as FeCl₄⁻,⁴¹ Nb₆Cl₁₈³⁻,^{42,43} Fe(C₂O₄)₃³⁻,^{44,45} have been engaged in order to create situations where localized magnetic moments will coexist in the inorganic anionic lattice with conduction electrons delocalized on the organic slab, as exemplified in the superconductor (BEDT-TTF)₄[(H₂O)Fe(C₂O₄)₃]·PhCN. In that respect, the comparison of isostructural salts of GaCl₄⁻ (non-magnetic) and FeCl₄⁻ ($S = 5/2$) is particularly interesting.⁴⁶ For example, whereas λ -(BETS)₂FeCl₄ becomes insulating below 8.5 K,^{47,48} its gallium analogue is superconducting below 8 K.^{49,50}

Furthermore, the development of a solution chemistry of large, isostructural and isosteric chalcogenide metal cluster anions such as Re₆Q₅Cl₉⁻,⁵¹⁻⁵³ Re₆Q₆Cl₈²⁻,^{53,54} (Q = S, Se), has offered unique opportunities for the construction of novel families of cation radical salts based on TTF, TMTTF, DTTTF, or BEDT-TTF. Of particular interest is the series of two-dimensional phases formulated as β -(BEDT-TTF)₄[Re₆Q₆Cl₈](solvent), (Q = S, Se; solvent = DMF, THF, dioxane, H₂O), whose macroscopic metallic properties may be fine-tuned from the neutral molecular (solvent) guest site upon significant manipulation of the collective response of a precise

set of C–H _{π} -donor \cdots O_{guest} hydrogen bonds.^{54,55} Polyoxometalate anions also offer a large number of counteranions of various shapes and magnetic states for the elaboration of molecular materials by electrocrystallization, as recently reviewed by Coronado and Gómez-García.⁵⁶ For example, the prototypical salt and formulation (BEDT-TTF)₈SiW₁₂O₄₀,⁵⁷ with alternating organic and inorganic layers, is consistently obtained by electro-oxidizing BEDT-TTF in the presence of the α -Keggin [SiW₁₂O₄₀]⁴⁻ anion and a number of its derivatives. In addition, a wide range of closed-shell ammonium counter cations have been used in radical anion salts of dithiolenes such as Ni(dmit)₂⁻ (see below). Such examples include Me₄N⁺,⁵⁸ ⁺NMe₃-(CH₂)₄Me₃N⁺,⁵⁹ and C(NMe₂)₃⁺.⁶⁰

Electroactive Molecules. Electrocrystallization has been most successfully applied with organic π -donor molecules such as arenes (fluoranthene, perylene) and tetrathiafulvalene derivatives. The former afford very soluble, albeit somewhat unstable, cation-radical salts which therefore require low-temperature electrocrystallization conditions.^{61,62} On the other hand, tetrathiafulvalene-based molecules give rise to stable cation-radical salts with low solubility constants in weakly polar solvents (CH₂Cl₂, THF). Electrocrystallization experiments are often successful, but will always require, for every donor/anion couple, an optimization of the electrolysis conditions.

The discovery of superconductivity in Bechgaard salts was the starting point of a vigorous synthetic effort from organic chemists to imagine and synthesize new donor molecules.⁶³ The numerous synthetic routes investigated essentially include the heteroatom substitution in the TTF core, i.e., S vs Se vs Te, and the functionalization of the TTF (or TSF) core with alkyl, thioalkyl, or other such substituents. In that respect, BEDT-TTF (Chart 1), with a redox core of larger spatial extension and twice as many sulfur atoms as TTF, increasing its capacity to engage in intermolecular transverse interactions in the solid state, proved to be particularly successful in electrocrystallization experiments. Thus, the prominent donor molecule of the first class of novel two-dimensional organic metals and superconductors, symbolized by β -(BEDT-TTF)₂I₃⁶⁴ (BEDT-TTF = bis-(ethylenedithio)tetrathiafulvalene), has been engaged with a large variety of anions (see above).³⁵ Note that the somewhat lower solubility of neutral BEDT-TTF or its analogues, when compared with TMTTF or TMTSF, compelled chemists to look for alternative electrocrystallization solvents such as 1,1,2-trichloroethane. The quality of this commercially available solvent, however, is not always satisfactory and requires careful purification.

More recent developments in the conception and preparation of novel donor molecules involve asymmetric donors, molecules of increased spatial extension, dimeric donors, and molecules bearing an extra functionality. Let us describe them in more details. Most of the TTF-like molecules are centrosymmetric, mainly because of their preparation procedures which involve the symmetric coupling of two identical halves to form the central C=C double bond. The development of asymmetrical coupling procedures⁶⁵ allowed for the preparation of noncentrosymmetric donor molecules,

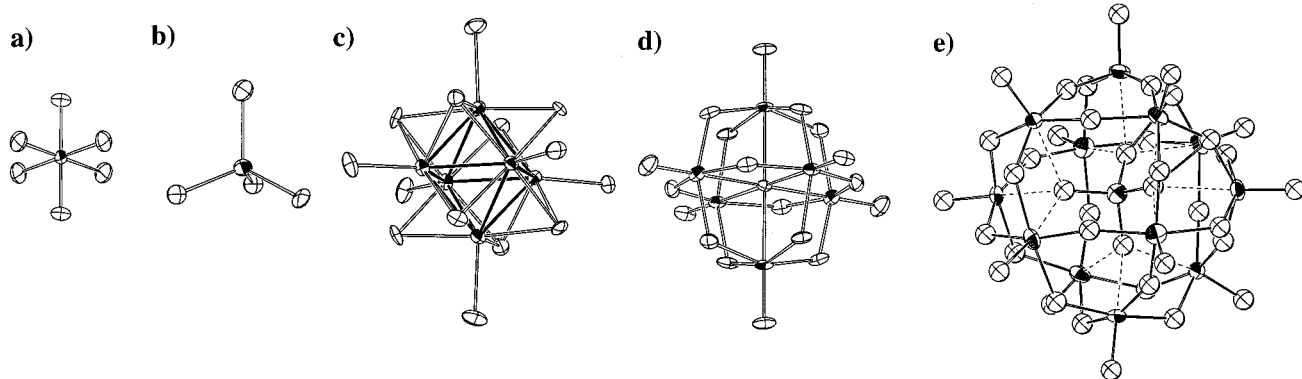
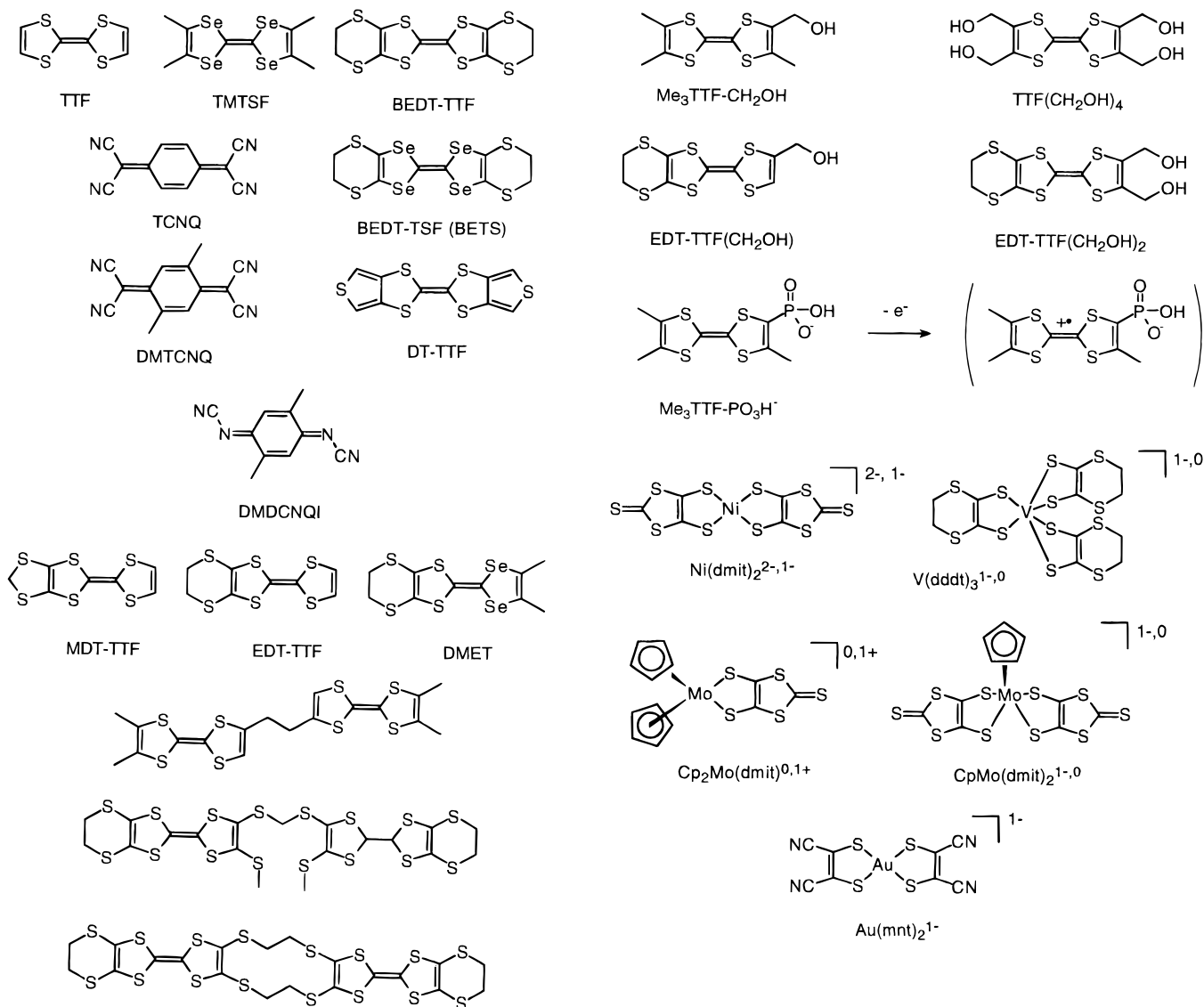


Figure 5. Comparison of the size and shape of a selection of anions used in electrocrystallization experiments and drawn at the same scale: (a) AsF_6^- , (b) FeCl_4^- , (c) $\text{Re}_6\text{S}_6\text{Cl}_8^{2-}$, (d) $\text{Mo}_6\text{O}_{19}^{2-}$, and (e) $\text{SiW}_{12}\text{O}_{40}^{4-}$.

Chart 1



such as EDT-TTF, in macroscopic quantities.⁶⁶ These dissymmetrical molecules were often found to crystallize into inversion-related dimers, favoring the so-called two-dimensional κ -phase arrangement, as found in the $(\text{MDT-TTF})_2\text{AuI}_2$ and $(\text{DMET})_2\text{AuBr}_2$, which both become superconducting.^{67,68}

π -Donors of larger spatial extension have been recently reviewed and will be discussed only briefly here.²

Albeit molecules such as BDT-TTFH₂ or BDT-TTP are reminiscent of TTF, their HOMO differs strongly from that of TTF, with apparition of larger coefficients on the outer carbon atoms of the TTF core (Figure 6). In addition, a decrease in the oxidation potential, when compared with TTF, is observed, as well as a destabilization of the cation radical species with respect to the diamagnetic neutral and dicationic forms. Several

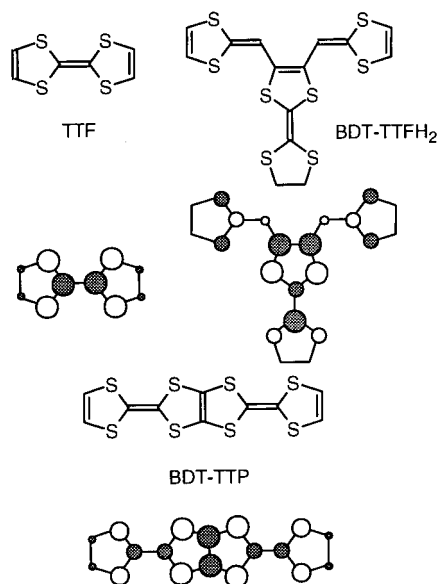


Figure 6. Symmetry of the HOMOs of TTF, BDT-TTFH₂, and BDT-TTP.

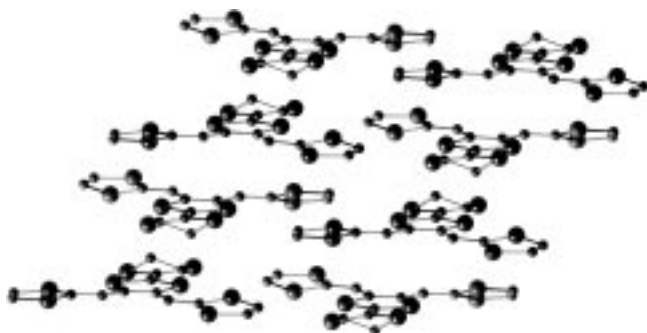


Figure 7. A view of the 2D mode of stacking in (BDT-TTFH₂)(ClO₄).⁸³

metallic and superconducting salts were obtained by Misaki et al. by electrocrystallization of BDT-TTP and its analogues.⁶⁹

The extended tetrathiafulvalene analogue, BDT-TTFH₂, was shown to afford a 1:1 salt with ClO₄⁻ with a novel fascinating mode of overlap of the T-shape molecules (Figure 7).⁷⁰ Head-to-tail dimers stack along the *c*-axis, while the outer dithiafulvenyl rings interleave along the *b*-axis, giving rise to an unprecedented two-dimensional pattern. It should be pointed out that these rigid extended donors are often quite insoluble in usual solvents, and therefore, electrocrystallization experiments may have to be conducted at elevated temperatures (40–50 °C) in solvents with higher boiling point such as PhCl or PhCN. The salts formed at the anode are also very insoluble in these media and precipitate too rapidly on the electrode unless very low current densities are used (0.1 μA/cm²).

Recently, a variety of donor molecules involving two tetrathiafulvalene moieties linked together by organic (–CH₂CH₂–, –CH=CH–, –C≡C–) or organometallic (–S–, –SS–, –Te–, –TeTe–, –Me₂Si–, –PhP–, –Hg–, etc.) spacers have been described.⁷¹ Despite this synthetic effort, only a few molecules were successfully electrocrystallized,^{72,73} for example, the bis(3,4-dimethyltetrathiafulvalen-3'-yl)ethane with the AsF₆⁻ anion⁷⁴ or with anionic Re₆-cluster anions such as Re₆S₅Cl₉⁻.²⁴

These molecules have the potential to form parallel, covalently linked, albeit weakly coupled, radical-cation stacks or slabs, giving rise to multiband conducting organic systems,⁷⁵ an issue of current intense interest, as demonstrated earlier in the TTF[Ni(dmit)₂]₂ system.^{76,77} In the Re₆S₅Cl₉⁻ salts with bis(3,4-dimethyltetrathiafulvalen-3'-yl)ethane, it was shown that the orbital degeneracy of the two TTF moieties system was removed by less than 0.1 eV. Since the HOMO of an individual TTF moiety is mainly localized on the central sulfur and carbon atoms with small contributions of the outer carbon atoms, it is expected, and indeed observed in electrochemical measurements, that through-bond interactions between the two TTF moieties remain weak while through-space interactions will mainly depend on the geometry of the bridge.⁷⁸

In most of the structures described above, overlap interactions between open-shell molecules compete only with close-packing requirements and van der Waals interactions to control the final solid-state arrangement of the salts. It is therefore tempting to purposely introduce into such constructions additional intermolecular interactions such as hydrogen bonding. While numerous molecules bearing hydroxyl, amino, amide, or thioamide^{66,79} substituents have been prepared, only a few have been engaged in cation-radical salts.

The facile and selective lithiation of trimethyltetrathiafulvalene allowed the preparation of several Me₃TTF cores functionalized with CO₂H, CH₂OH, and C*(OH)Me substituents.^{80,81} EDT-TTF bearing one or two CH₂OH groups was also prepared by reduction of the corresponding esters or aldehydes and engaged in electrocrystallization experiments, particularly with oxide anions such as ClO₄⁻, ReO₄⁻, Mo₆O₁₉²⁻ or heteropolyanions such as [PW₁₂O₄₀]³⁻ or [SiW₁₂O₄₀]⁴⁻, to favor hydrogen-bond interactions between hydroxymethyl-functionalized donors and the most basic oxygen atoms of the anions. In those electrocrystallization experiments, polar solvents (TCE + EtOH 10%, CH₃CN, DMF, and mixtures thereof) are often necessary in order to dissolve both the hydroxylated donors and the oxide anions. The carboxylic acid derivative Me₃TTF–CO₂H indeed forms centrosymmetric dimers in the solid state, but its electrooxidation to the radical cation in a CH₃CN/DMF mixture results in a decarboxylation process and electrocrystallization of the Me₃TTF⁺ cation instead.⁸² In the 2:1 salt of EDT-TTF(CH₂OH) with ClO₄⁻ and ReO₄⁻, the OH group is found to be directed toward one of the oxygen atoms of the tetrahedral oxide anion and the subsequent orientation effect of the anion allows for the formation of a κ-type arrangement (a 2D chessboard like pattern of interacting dimers; see Figure 4) of the organic donor slab in the solid state, which in turn gives rise to a two-dimensional electronic structure.⁸³ An even stronger organizing effect of (OH)_{donor}...O_{anion} hydrogen-bond interactions is shown in Figure 8 for the Mo₆O₁₉²⁻ salt of bis(hydroxymethyl)(ethylenedithio)tetrathiafulvalene, EDT-TTF(CH₂OH)₂. Donor molecules organize into dimers strongly associated through one face of the Mo₆O₁₉²⁻ anion, affording a supramolecular neutral parallelepipedic unit, [EDT-TTF(CH₂OH)₂]₂⁺(Mo₆O₁₉²⁻), whose close packing defines the final solid-state arrangement.⁸⁴ A recent and salient example of a network of precise and cooperative

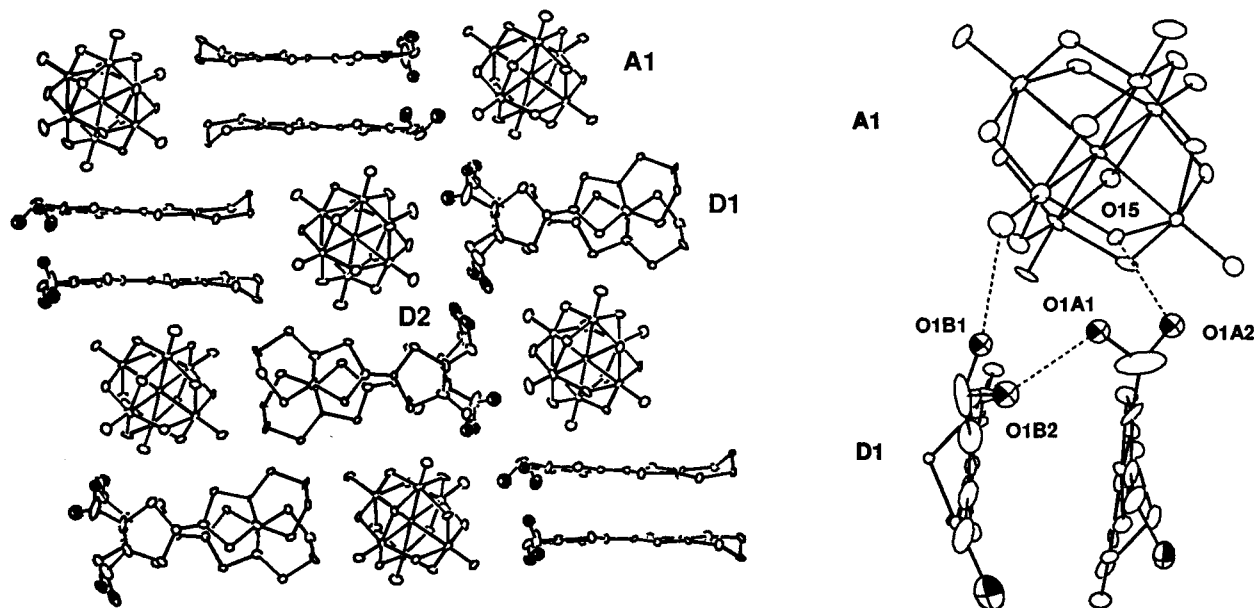


Figure 8. Solid-state architecture of $[\text{EDT-TTF}(\text{CH}_2\text{OH})_2]_2\text{Mo}_6\text{O}_{19}$, showing the hydrogen-bond interactions between hydroxyl groups of the donor molecules and the oxygen atoms of one face of the $\text{Mo}_6\text{O}_{19}^{2-}$ polyanion.⁸⁴



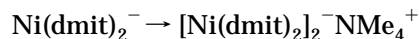
Figure 9. The layered, zwitterionic radical $(\text{Me}_3\text{TTF}^+)\text{PO}_3\text{H}^-$. The larger dark spheres represent the O atoms of the PO_3H^- substituents engaged in the hydrogen-bond network.⁸⁵

hydrogen bonding is also provided by the neutral zwitterionic radical obtained by electrocrystallization of a closed-shell anilinium phosphonate salt, $[\text{PhNH}_3]^+[\text{Me}_3\text{TTF-PO}_3\text{H}]^-$.⁸⁵ Its structure (Figure 9) reveals the presence of hydrogen-bonded molecular ribbons interleaved into a novel layered architecture whose two-dimensional electronic structure is similar to that of the prototypical two-dimensional metal and superconductor β -(BEDT-TTF) $_2\text{I}_3$,^{64b} based on a π -donor molecules of larger spatial extension.

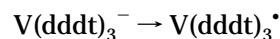
Electrochemical *reduction* of π -acceptor molecules such as TCNQ or dimethyldicyanoquinodimide, DMD-CNQI, has allowed radical anion salts of 1:1 stoichiometry such as $[\text{Cp}^*\text{Fe}^+][\text{TCNQ}^{\cdot-}]$ ¹⁹ and salts of 1:2 stoichiometry such as $[\text{DMDCNQI}]_2\text{Cu}$ ⁸⁶ to be obtained. The latter is a rare example of a radical-anion-based metallic conductor whose three-dimensional architecture, based on diamantoid forms of the coordination polymer build around the copper atoms,⁸⁷ prevents the appearance of any structural or electronic transitions toward a localized, insulating state.

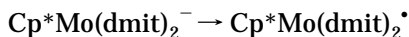
Finally, electrocrystallization is not just restricted to oxidation (or reduction) of organic molecules, it has also been extensively used for electroactive dithiolene metal complexes⁸⁸ or mixed cyclopentadienyl/dithiolene complexes.⁸⁹

Because of their capability to generate strong intermolecular interactions, as demonstrated by the remarkable solid-state chemistry of the inorganic molecular conductor and superconductor $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$,^{76,77} dithiolene ligands such as dmit^{2-} and dddt^{2-} have recently been used in the synthesis of novel metal complexes. Depending on the charge of the electrocrystallized complex, various types of materials can be obtained. Oxidation of anionic complexes sometimes leads to mixed valence conducting salts



or to neutral radicals^{90,91}

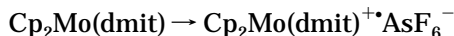




Similarly oxidation of neutral complexes affords mixed valence cationic salts⁹²



or 1:1 radical cation salts⁹³



Note that the electrocrystallization need not be restricted to the preparation of conducting systems. Several examples described above yield insulating radical salts that can have interesting low-dimensional magnetic properties such as spin chains⁹⁴ or spin ladders, as for (BEDT-TTF)[Zn(SCN)₃],⁹⁵ (DT-TTF)₂[Au(mnt)₂],⁹⁶ and [Cp₂M(dmid)][TCNQF₄] (M = Mo, W) (dmid²⁻ = 2-oxo-1,3-dithiol-4,5-dithiolate),⁹⁷ or even exhibit 3D antiferromagnetism ground states (Figure 10).^{93,98,99} Not only planar donor or acceptor molecules are amenable to electrocrystallization; any electroactive molecule can be used, as shown by the examples of salts based on globular π -donor molecules such as a cryptophane E (isolated in its monocationic form¹⁰⁰), a sodium cryptate whose reduction affords a radical zwitterion,¹⁰¹ or C₆₀, whose electrochemical reduction¹⁰² afforded for example alkylammonium⁻,¹⁰³ tetraphenylphosphonium⁻,¹⁰⁴ and transition metal chelate-Fulleride compounds.¹⁰⁵

Recent Developments

Toward Control of the Stoichiometry. To control the stoichiometry of the electrocrystallized compound, different electrocrystallization conditions can be used. As shown below in the BEDT-TTF vs PF₆⁻ system, the *galvanostatic* mode with low current intensity is most often used for mixed valence compounds ($\rho < 1$)



while the 1:1 salt has been obtained in the *potentiostatic* mode at a working potential above the first oxidation potential of BEDT-TTF³³



Furthermore, the *galvanostatic* electrolysis of BEDT-TTF in an oxidizing solution of ClCH₂COCl was reported to afford the dicationic BEDT-TTF²⁺.¹⁰⁶



A Synthetic Tool for Coordination Polymer Chemistry. As demonstrated in the preceding sections, the technique of electrocrystallization allows assembly of open-shell molecules, be they neutral or charged, into high-quality single crystals. It is also a tool for promoting novel associations in coordination chemistry. For example, the electrocrystallization of TMTSF with a mixture of quaternary ammonium salts of PF₆⁻ and TaF₆⁻ afforded a salt with the bimetallic anion Ta₂F₁₁⁻.¹⁰⁷ The analysis of the structure of the superconducting phase κ -(BEDT-TTF)₂(Cu[N(CN)₂]Br)¹⁰⁸ reveals the pres-

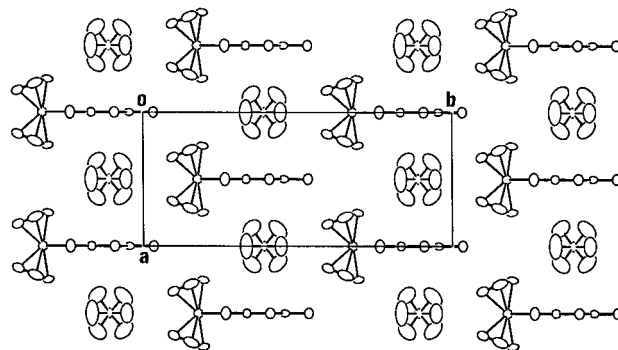


Figure 10. Structure of Cp₂Mo(dmit)⁺AsF₆⁻. In this insulating compound, the magnetic moments localized on the dithiolene ligands are antiferromagnetically coupled below 8 K⁹³

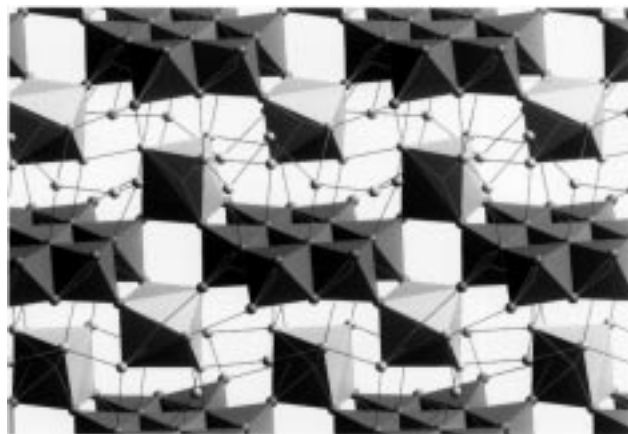


Figure 11. κ -(2/3-3)-(EDT-TTF)₈⁴⁺{[Ca(H₂O)₄]₂(TeW₆O₂₄)·7H₂O}₂⁴⁻. A view of a single inorganic slab revealing the 2D polymeric array constructed from the Ca²⁺ first and second coordination spheres and the crownlike Anderson hexaanions.¹⁰⁹ The water coordination net is represented by the set of thin lines encompassing all separations between oxygen atoms shorter than 3.0 Å.

ence of a 2D coordination polymer (Cu[N(CN)₂]Br⁻)_n formed upon electrocrystallization of BEDT-TTF in the presence of CuBr and PPh₄⁺[N(CN)₂]⁻ in trichloroethane. The electrocrystallization of EDT-TTF in the presence of the Anderson [TeW₆O₂₄]⁶⁻ heteropolyanion, together with CaCl₂ yielded a bicontinuous hybrid composite, κ (2/3-3)-(EDT-TTF)₈{[Ca(H₂O)₄]₂(TeW₆O₂₄)·7H₂O}₂ (Figure 11) whose structure revealed a 2D copolymerization of the crown-shaped Anderson polyoxotungstate hexaanions and water clusters within the alkaline-earth first and second coordination spheres.¹⁰⁹ Finally, one should emphasize the potential of the electrocrystallization technique for the synthesis of inorganic polymers, as exemplified by the observation that the multiple metal-metal bond within the dinuclear complex [Rh₂(MeCN)₁₀](BF₄) can be induced to polymerize upon reduction at the electrode into single crystals containing an infinite 1D metal-metal bonded array, formulated {[Rh(MeCN)₄](BF₄)_{1.5}]_∞ (Figure 12), the first mixed-valence 1D compound of rhodium.¹¹⁰

Binary but also Ternary Salts. Ternary salts involving three different ions can also be prepared by electrocrystallization when, for example, a donor is oxidized in the presence of two counteranions simultaneously. Thus, ternary phases such as [TTF⁺]₃-[Re₆S₆Cl₈²⁻][Cl⁻] or [TTF⁺]₃[Mo₆Cl₁₄²⁻][X⁻] (X⁻ = Cl⁻, Br⁻, I⁻) were purposely induced to electrocrystallize

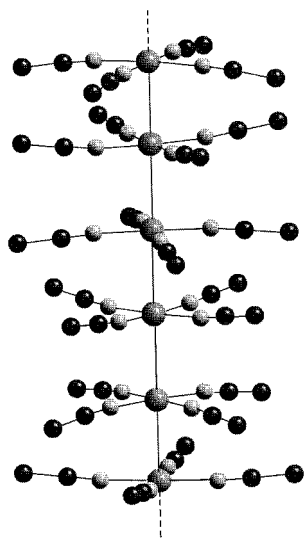


Figure 12. A $[\text{Rh}_6(\text{MeCN})_{24}]^{9+}$ segment of the infinite 1D metal-metal bonded chains which polymerize during the cathodic electrocrystallization of $[\text{Rh}_2(\text{MeCN})_{10}](\text{BF}_4)$.¹¹⁰

and shown to adopt an anti-perovskite structure exhibiting an antiferromagnetic ground state at low temperature.^{98,99} When the electrocrystallization experiments are performed without the halide salt, the paramagnetic mixed valence binary salt $[(\text{TTF}^+)_{2}(\text{TTF}^0)][\text{Re}_6\text{S}_6\text{Cl}_8^{2-}]$ crystallizes out instead.¹¹¹ Similarly, the ammonium or phosphonium cation present in the electrolyte might also crystallize out, together with the electroactive species and the anion, as observed for example in the TTF salt of the paramagnetic cluster anion $\text{Nb}_6\text{Cl}_{18}^{3-}$, which incorporates Et_4N^+ cations.⁴²

Redox States and Molecular Conformation. The electrocrystallization method also enables ordered associations of species of low stability to be formed, and hence their structures to be determined. Thus, structural modifications that are induced by the loss of one electron can be studied, as observed in the mixed cyclopentadienyl/dithiolenes complexes.⁹¹ A very nice example is also provided by [10]- and [12]-tetrathiafulvalenophanes, whose conformation switches from trans to cis when the neutral molecule is oxidized into a radical-cation (Figure 13).⁵³

Toward a Molecular Metallurgy: Doping Solid Solutions. The high purity of materials obtained by electrocrystallization enables the introduction of disorder or molecular defects in a controlled fashion by doping strategies or by forming molecular alloys. This is particularly interesting for *isostructural* materials, whose electronic properties vary with the nature of the molecular ions. Furthermore, the intrinsic disorder introduced by the solid solution plays a crucial role on the dynamics of the conduction electrons. In cation-radical salts, two possibilities are offered, alloying the donor (TMTTF vs TMTSF) or alloying the counteranion (ClO_4^- vs ReO_4^- ; PF_6^- vs AsF_6^- vs SbF_6^-). Electrocrystallization of solid solutions of two different donors proved problematic because of differences in the oxidation potentials of the two donors and solubility differences of the two pure salts which might favor one pure phase over the alloy. In the low concentration limit,^{112,113} it was shown, for example, that doping $(\text{TMTSF})_2\text{ClO}_4$ with less than 1% TMTTF (note that $(\text{TMTTF})_2\text{ClO}_4$ is

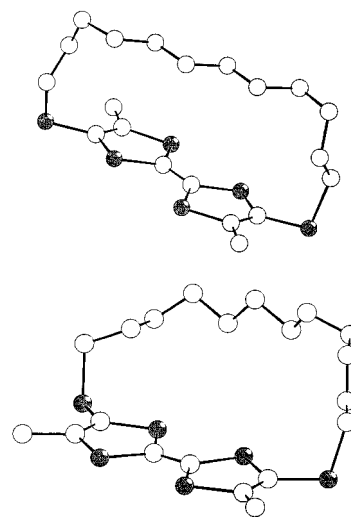


Figure 13. Trans-cis switch of [12]-tetrathiafulvalenophane upon oxidation. The trans conformation of the neutral molecule (top) switches to cis in its cation radical salt with $\text{Re}_6\text{S}_6\text{Cl}_8^{2-}$ (bottom).⁵³

a poor conductor which localizes below 200 K) destroys the superconductivity in $(\text{TMTSF})_2\text{ClO}_4$. In TMTSF/TMTTF solid solutions of the perrhenate salt $[(\text{TMTTF})_{1-x}(\text{TMTSF})_x]_2\text{ReO}_4$, $0 \leq x \leq 1$, the evolution with x of the electronic and structural properties deviates strongly from linearity due to a well-defined ordering of alternating TMTSF and TMTTF molecules for $x \approx 0.5$.¹¹⁴

Solid solutions of two different anions, such as in $(\text{TMTSF})_2(\text{AsF}_6)_{1-x}(\text{SbF}_6)_x$, $0 \leq x \leq 1$, whose composition (electron microprobe analysis) and structural properties (unit cell parameters and volume) vary linearly with x are much easier to synthesize. The introduction of such weak nonmagnetic disorder in these metallic salts enhances strongly the pinning of the spin density wave.¹¹⁵ Introduction of magnetic disorder by substituting a fraction of the diamagnetic tetrahedral GaCl_4^- anions by the high spin species ($S = 5/2$)¹¹⁶ FeCl_4^- is also of interest and has been successfully conducted in $(\text{BEDT-TSF})_2(\text{FeCl}_4)_{1-x}(\text{GaCl}_4)_x$ solid solutions. The pure salts are isostructural;¹¹⁷ in the solid solutions, the antiferromagnetic ground state of the FeCl_4^- salt competes with the superconducting state of the pure GaCl_4^- salt.¹¹⁸ Such competing collective behaviors can be readily investigated in such solid solutions by an analysis of the evolution of structural transitions. For example, the pristine $(\text{TMTSF})_2\text{X}$ series with $\text{X} = \text{ClO}_4^-$ and ReO_4^- are known to exhibit an anion ordering transition with two different critical wave vectors, $[\mathbf{q}_1 = (1/2, 1/2, 1/2)]$ and $[\mathbf{q}_2 = (0, 1/2, 0)]$, respectively]. The basic features of the (T, x) phase diagram in the $(\text{TMTSF})_2(\text{ReO}_4)_{1-x}(\text{ClO}_4)_x$ solid solutions was accounted for by a mean-field treatment of the Ising model (used in the pure salts to account for the two possible orientations of the tetrahedral anion located on an inversion center) with random interactions.¹¹⁹

Crystalline Thin Films. An important direction of research is the recent trends exemplified by the work of Ward and co-workers aimed at obtaining thin crystalline films of $(\text{BEDT-TTF})_2\text{I}_3$ on highly oriented pyrolytic graphite.¹²⁰ Indeed, there is a need to develop our ability to manipulate thin films of such electro-, photo-,

or magnetoactive crystalline, long-range-ordered molecular systems of high purity to construct devices for applications in information and sensor technologies as well as for investigating quantum size effects in condensed matter physics. An earlier step in this direction had been taken by Thakur et al., who reported¹²¹ the growth of thin crystalline films of (BEDT-TTF)₂Cu-(NCS)₂ brought about by forcing the electrocrystallization to occur within the interface of two opposing substrates. It should be emphasized that the surface and purity of the thin crystals grown in the latter, modified electrocrystallization experiments appear to be consistently of high quality, as demonstrated by scanning tunneling microscopy.

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