

## Introduction

When I was invited by M. G. Kanatzidis, Editor of the *Journal of Solid State Chemistry*, to be the Guest Editor for a special issue of this journal devoted to the subject of molecular metals, I was pleased and flattered: pleased, because this subject is my main research interest; flattered, simply because I had been selected as the Guest Editor. I appreciated the invitation all the more because almost every 5 years or so since I entered the field around 1980, some *well-disposed* science evaluators would point out to the decline and predict the fall of the research effort on molecular metals. Therefore, I considered the proposal of the *Journal of Solid State Chemistry* to dedicate the 2002 thematic special issue in hot topical areas to molecular metals a well-deserved recognition.

Predictions concerning the possible existence of conducting organic solids were made by McCoy [1] in 1911 and Kraus [2] in 1913. However, the experimental saga actually began in the 1950s with the seminal works on a perylene bromide salt by Akamatu *et al.* [3] and on several TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane)-containing electron transfer salts by workers at Du Pont [4], who were the first to report high conductivity for molecule-based solids. Ironically, note that the true first molecule-based metallic conductor was serendipitously prepared more than 150 years ago by Knop [5] by oxidizing potassium tetracyanoplatinate  $K_2[Pt(CN)_4]$  with chlorine or bromine, but the metal-like conductivity of the resulting “copper-shining” material, later called KCP, was measured only 30 years ago [6]. Together with the electron transfer salts of TCNQ, salts of TTF (TTF = tetrathiafulvalene) [7] were also shown to exhibit high conductivities [8]. Metal-like conductivity was first reported for [NMP][TCNQ] (NMP = *N*-methylphenazinium) near room temperature [9], and [TTF][TCNQ] extended the temperature range for metal-like conductivity down to 53 K [10].

Thus, the period between the early 1950s and the early 1970s could be compared to the “bronze age” or to the period when humans learned how to grow vegetables. At the end of this period, one could assert that:

### Molecular metals do exist!

Soon after, however, even though a large number of molecular metals were prepared and studied, some

lips-pursing Cassandras had already begun to spread some doubts:

### Just metals, so what?

In fact, as early as 1964, Little [11] suggested that appropriate one-dimensional (1-D) organic polymers could become superconductive at high (room) temperatures. From the early 1970s, clearly, metal-like conducting behavior was not enough and the new challenge was superconductivity. We had to wait until 1980 to celebrate the birth of the first molecular superconductor:  $(TMTSF)_2(PF_6)$  (TMTSF = tetramethyltetraselenafulvalene) was the first electron transfer salt to become superconductive under pressure [12] and  $(TMTSF)_2(CIO_4)$  was the first ambient-pressure superconductor [13]. A number of other modifications of TTF, such as the most famous BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene), also yielded molecular superconductors, as a matter of fact more than 100 to date [14]. The use of electron transfer salts based on inorganic coordination compounds, especially transition metal complexes, as components for metals and superconductors has been likewise extensively explored and several superconductors based on the  $M(dmit)_2$  complexes ( $dmit^{2-} = 2$ -thioxo-1,3-dithiole-4,5-dithiolato) have been characterized [15].

Following this burst of discoveries, from 1980 to 1986, we enjoyed a kind of golden age:

### Molecular superconductors do exist!

As time passed, the critical temperature  $T_c$  remained relatively low (less than 12.8 K at 0.3 kbar observed in  $\kappa$ - $(BEDT-TTF)_2Cu[N(CN)_2]Cl$  [16]) and in 1986, some “powder-grinding-backing” guys discovered the high- $T_c$  superconducting copper oxides [17]. A number of people left the field, and the molecular superconductor stock exchange seemed doomed to plunge. Then in 1991 came what could have been considered another blow: the discovery of the superconducting doped fullerenes [18] (although these compounds can also be considered molecular systems; see the papers by S. Margadonna and K. Prassides and R. N. Lyubovskaya and colleagues in this issue). Finally, workers at Bell Labs have recently claimed that one could turn any rock (i.e., pentacene in that case) into a superconductor by injecting charges in the surface in a field effect transistor (FET) device [19].



**Arx tarpeia Capitoli proxima! [20]**

Do not fear, molecular metals companions, “enter in hope” [21], as we will be around, and around, and around, ... for a while. We are certainly facing difficulties in the development of our research effort, namely, (i)  $T_c$  is still below 12.8 K; (ii) we are still more or less confined in what F. Wudl calls the “TTF-world”; and (iii) behaviors that seemed to be well established are now discovered to be sample-dependent in such a way that one might feel it necessary to produce “less quality crystals,” etc. Yet, our field is living still: just have a look at the attendance at the last International Symposium on Organic Metals in Rusutsu (Hokkaido) in September 2001, or at the last International Conference on Synthetic Metals in Bad-Gastein in July 2000. What might be the reasons for this survival and its promises? Some explanations may be the following: The area of molecular conductors is essentially basic-science-oriented, primarily interested in concepts and theories and in checking them by preparing new systems. Thus, some of us today might have funding problems, but we are not dependent on fad and fashion. Consequently, our community has developed a unique expertise and this allows excellent training for students and newcomers. Indeed, a number of people now working in the fields of the high- $T_c$  superconducting copper oxides, fullerenes, and FET came from our ranks and brought this unique expertise to those new fields, behaving as young queen bees starting new colonies with the wisdom of the mother queen.

In addition to the core of the subject matter of this issue, i.e., the preparation of molecular (super)conductors, several questions (together with those that will come up in the future) remain to be addressed, giving rise to new challenges:

*What about the TTF-world confinement?* No sweat, this world still seems today to be infinite. In fact, more than half of the 41 papers in this issue deal with compounds derived from TTF-like molecules (and 8 deal with systems derived from metal complexes). One might question the interest of such variations on the same theme. For example, the simple replacement of S atoms with Se atoms in a TTF-like donor molecule could be considered another futile synthesis achievement. Nevertheless, consider the BETS (bis(ethylenedithio)tetraselenafulvalene) donor, which is derived from BEDT-TTF by replacing 4 S atoms of the central TTF fragment of BEDT-TTF with 4 Se atoms: it happened that interplay of conductivity and magnetism could be observed for the first time in a BETS-derived compound, the  $\lambda$ -(BETS) $_2$ FeCl $_4$  phase [22]. The design of a single-component neutral molecular metal is another illustration: in a visionary article of 1997 [23], E. Canadell dreamed of it, and in 2001, A. Kobayashi and co-workers did it

by synthesizing a hybrid of TTF and M(dmit) $_2$ , Ni(tm $dt$ ) $_2$  (tm $dt$  = trimethylenetetrathiafulvalenedithiolate) [24].

*Interplay of properties.* Today, one may consider that molecule-based conductors and superconductors have become non-rare materials. Thus, the development of multifunctional molecular systems has evolved as a new challenge. In these systems, the coexistence of several properties (for example, conductivity and magnetism [22] or conductivity and photochromism), and better still an actual interplay between these properties, is much sought after. Several papers along this line may be found in this issue (T. Sugimoto and co-workers, L. Ouahab and co-workers, J. Yamada and co-workers, A. Miyazaki *et al.*, C. Rovira and colleagues, E. Coronado and colleagues).

*Materials processing.* To evaluate the potential use of molecular conductors (in future electronic device applications, for examples), one needs to process this material in a usable form, such as a thin film or a wire. Two papers in this issue (J. Fraxedas *et al.*, L. Valade *et al.*) address this question.

It is obvious that all the achievements in the area of molecular conductors could not have been obtained without collaboration with the physicists. In his microreview, J. Singleton will explain why (happily) physicists love molecular metals. If the area of molecular metals is, as said above, mostly basic-science-oriented, this does not mean that applications are not also aimed at, as illustrated by the microreview by R. Metzger.

In conclusion, after more than 20 years in the molecular conductor business and before my approaching farewell, I am still convinced that this area has a great future. Consequently, I have no second thoughts about wishing good luck to those who will carry the torch further. They must only remember that “ce n’est pas la peur d’entreprendre, c’est la peur de réussir qui explique plus d’un échec” [25].

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Patrick Cassoux  
Guest Editor