

# Electrochemical Synthesis of New One-Dimensional Metals: Radical Salts of Perylene

H. J. Keller, D. Nöthe, H. Pritzkow, D. Dehe, M. Werner, R. H. Harms,\* P. Koch and D. Schweitzer

Anorganisch-Chemisches Institut der Universität Heidelberg, Heidelberg, Federal Republic of Germany and Max-Planck-Institut für Medizinische Forschung, Abteilung für Molekulare Physik, Heidelberg, Federal Republic of Germany

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## Abstract

*Electrochemical synthesis of new one-dimensional metals: Radical salts of perylene.* Keller, H. J.\*; Nöthe, D.\*; Pritzkow, H.\*; Wehe, D.\*; Werner, M.\*; Harms, R. H.\*; Koch, P.\*\*; Schweitzer, D.\*\* (Anorganisch-Chemisches Institut,\* Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Federal Republic of Germany and Max-Planck-Institut für Medizinische Forschung,\*\* Abteilung für Molekulare Physik, Jahnstrasse 29, D-6900 Heidelberg, Federal Republic of Germany).

The electrochemical synthesis of four highly conducting peryleniumyl salts is reported. The temperature dependence of the conductivity has been measured and exhibits a metallic regime between 200–300 K. The crystal structures of two of the compounds have been solved.

Various planar aromatic hydrocarbons (anthracene, tetracene, pyrene, perylene, coronene, etc.) were tested for their ability to form crystalline radical salts when oxidized at a platinum anode at constant potential. In order to find the appropriate conditions, different counterions ( $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{BF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ), solvents ( $\text{CH}_2\text{Cl}_2$ , THF), types of electrochemical cells, and potentials (2.5–6 V) were used in the experiments. With most of the tested hydrocarbons, only polycrystalline, black materials covering the electrode were formed; in many cases, no solid products were formed at all. The only molecule capable of growing needle-like, metallic crystals under these conditions was found to be perylene.

Highly conducting, crystalline solids were obtained by electrolyzing perylene in  $\text{CH}_2\text{Cl}_2$  or THF, using  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  or  $\text{Bu}_4\text{N}^+\text{AsF}_6^-$  as supporting electrolytes [1]. Elementary analysis revealed that each material contains different amounts of anions and solvent molecules, resulting in the following stoichiometries for compounds (1)–(4).



and thus suggesting a mixed valence state.

(1)–(4) form black, reflective needles up to several cm in size, which exhibit metallic conductivity along the needle axis, with values ranging from 70–1200  $\Omega^{-1} \text{cm}^{-1}$  at room temperature. The temperature dependence of the conductivity shows a metallic regime down to about 200 K and a thermally activated behaviour at lower temperatures. Typical curves for (1) and (2) are shown in Fig. 1 for crystals

grown from  $\text{CH}_2\text{Cl}_2$  solutions. The striking feature is a sudden drop of conductivity over about two orders of magnitude at 120 K and 110 K, respectively. This effect is not due to a breaking of the crystals, because it can be reproduced reversibly, only shifting the transition temperature to a somewhat higher value. Also, the initial room temperature conductivity shows some degradation during such temperature cycles.

In all batches grown from  $\text{CH}_2\text{Cl}_2$  solutions, thinner crystals with a slightly different analytical composition were found. These crystals and all crystals grown from THF solutions do not show the sharp transition described above. Instead, a gradual transition from a flat-curved to a linear behaviour is observed. Typical results for (3) and (4), grown from THF solutions, are shown in Fig. 2.

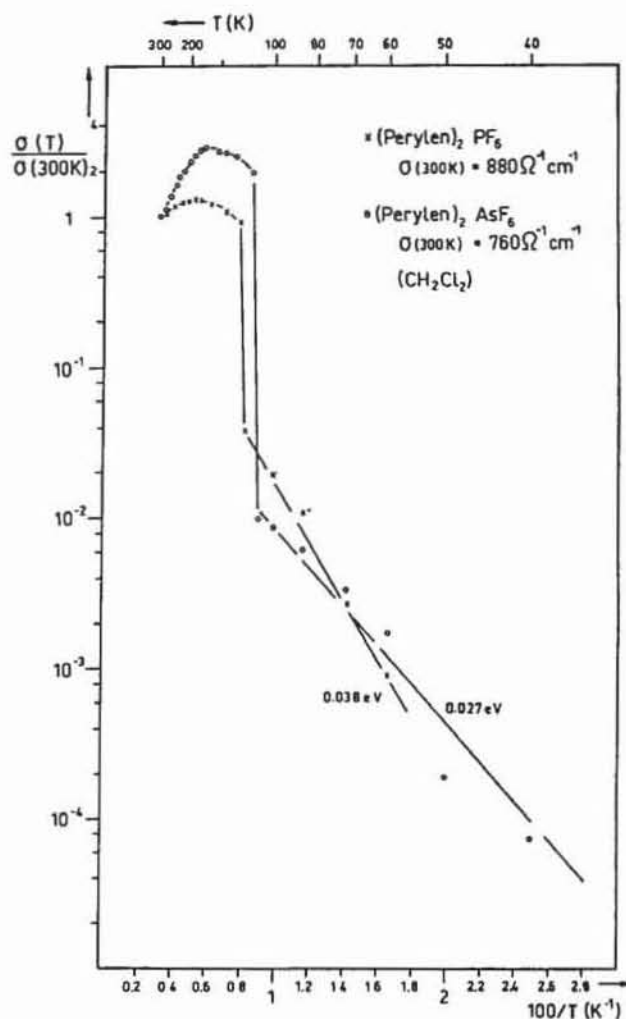


Fig. 1. Temperature dependence of the normalized DC conductivity of (1) and (2).

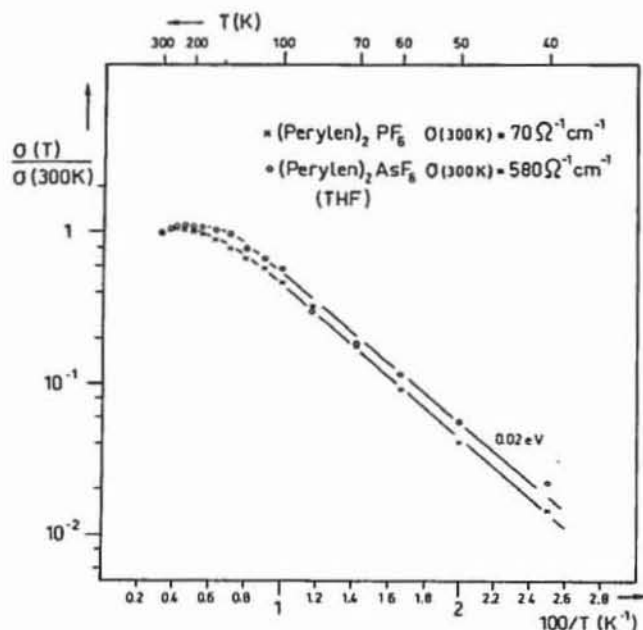


Fig. 2. Temperature dependence of the normalized DC conductivity of (3) and (4).

The crystal structures of (1) and (2) were solved by direct methods [1]. All crystals of (1)–(4) seem to be isostructural, with orthorhombic space group  $P_{2121}$ . Cell parameters are

$$a = 4.285 \text{ \AA}, b = 12.915 \text{ \AA}, c = 14.033 \text{ \AA} \text{ for (1) and}$$

$$a = 4.294 \text{ \AA}, b = 13.077 \text{ \AA}, c = 14.132 \text{ \AA} \text{ for (2).}$$

The perylene molecules form segregated stacks directed along the  $a$ -axis with interplanar spacings of 3.40 Å and an angle of 37.7° with respect to the  $bc$ -plane, illustrated in Fig. 3. The stacking arrangement is very similar to that found in the metallic  $(\text{pe})_2[\text{Pt}(\text{mnt})_2]$  [2].

The channels between stacks are filled by anions and solvent molecules ( $\text{CH}_2\text{Cl}_2$ ). With a ratio of 2:1 between perylene molecules and anions, every second cell should be occupied by an anion. However, the unstoichiometric ratio of 2:1.1 found from chemical analysis must produce some disorder effects in the anion channels. Consequently, atom positions for these species cannot be localized exactly and no correlation between different channels can be found. A complete description of all structural features will be published [1].

### Conclusion

The electrochemical oxidation of organic donor molecules can be used successfully in the search for new synthetic metals. This method selects the most highly conducting materials and provides a way of growing large single crystals. The peryleniumyl hexafluorophosphate and hexafluoroarsenate salts effectively demonstrate these advantages.

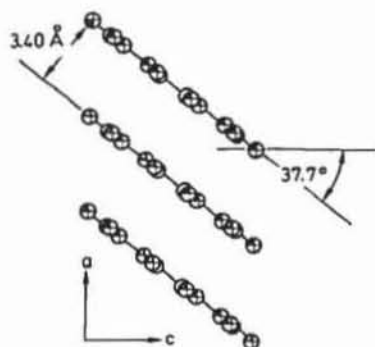


Fig. 3. Projection of a cation stack onto the  $ac$ -plane.

### References

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2. Alácer, L., Chasseau, D. and Gaultier, J., *Solid State Commun.* 1980, 35, 945.

Anorganisch-Chemisches Institut  
Universität Heidelberg  
Im Neuenheimer Feld 270  
D-6900 Heidelberg, Federal Republic of Germany

Max-Planck-Institut für Medizinische Forschung  
Abteilung für Molekulare Physik  
Jahnshasse 29  
D-6900 Heidelberg, Federal Republic of Germany