Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effect of the Solvent Used for Electrocrystallization of Organic Metals

Hiroyuki Anzai [a] , Madoka Tokumoto [a] & Gunzi Saito [b a]

[a] Electrotechnical Laboratory, Sakura-mura, Niiharigun, Ibaraki, 305, JAPAN

[b] Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo, 106, JAPAN

Version of record first published: 17 Oct 2011.

To cite this article: Hiroyuki Anzai , Madoka Tokumoto & Gunzi Saito (1985): Effect of the Solvent Used for Electrocrystallization of Organic Metals, Molecular Crystals and Liquid Crystals, 125:1, 385-392

To link to this article: http://dx.doi.org/10.1080/00268948508080118

Mol. Cryst. Liq. Cryst. 1985, Vol. 125, pp. 385-392
0026-8941/85/1254-0385/$15.00/0

Printed in the United States of America

EFFECT OF THE SOLVENT USED FOR ELECTROCRYSTALLIZATION OF ORGANIC METALS

HIROYUKI ANZAI and MADOKA TOKUMOTO
Electrotechnical Laboratory, Sakura-mura, Niihari-gun, Ibaraki 305, JAPAN

GUNZI SAITO
Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, JAPAN

Abstract The property of the organic solvents used for the electrocrystallization drastically affects the quality of the obtained crystals, and this point has been carefully investigated by using TTT, TMTTF, TMTSF and other reagents as the donor and several tetrabutylammonium salts as the supporting electrolyte.

INTRODUCTION

The study of organic metals strongly depends on whether good crystals can be obtained or not, as exemplified by the relation between the crystal growth of TMTTF-TCNQ[1] and its physical properties.[2-3] Electrocrystallization is one of the important methods to grow single crystals of organic metals. The property of organic solvents used for the electrocrystallization drastically affects the quality of the obtained crystals. We have carefully investigated this point.

EXPERIMENTAL

TTT, TMTTF, TMTSF and other reagents as the donor, and several tetrabutylammonium salts as the supporting electrolyte were used for crystal growth. The cell used for crystal growth consists of the outer and inner quartz vessels, a pair of Pt electrodes and Teflon caps as shown in Fig. 1. The crystal growth was carried out in the solution of about 5×10^{-5} M of donor and 2×10^{-4} M of the tetrabutylammonium salt dissolved in 40-80 ml of organic solvent; the current of 1-10 μA was applied at room temperature under an atmosphere of nitrogen gas for a period of about a month. The used reagents and solvents, and measured data for the obtained crystals are listed in Table I, and the pictures of the grown crystals are shown in Fig.2.

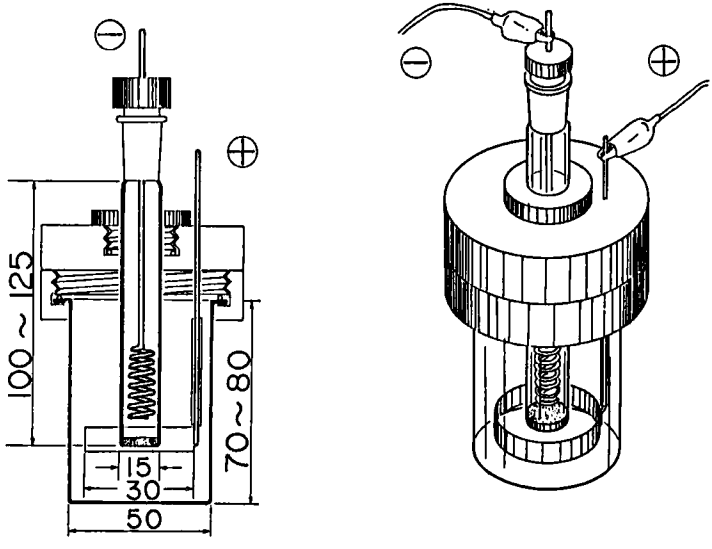

FIGURE 1. The crystal growth cell for electrocrystallization. Dimensions are in mm.

TABLE I The measured data for the obtained crystals.

Solvent	Donor	Bu_4NX (X=)	Cell Voltage (V)	Current (μA)	Crystal Size (mm^3)
THF	TTT	ClO_4	0.75	1.04	0.01x0.01x0.6
C_6H_5Cl	TTT	ClO_4	3.5	0.90	0.05x0.02x3.0
o-$C_6H_4Cl_2$	TTT	ClO_4	1.5	0.95	0.25x0.08x2.5
m-$C_6H_4Cl_2$	TTT	ClO_4	4.6	0.80	0.7x0.02x0.5
1,2,4-$C_6H_3Cl_3$	TTT	ClO_4	>10	0.4	0.1x0.05x2.2
$C_6H_5OCH_3$	TTT	ClO_4	5.0	1.72	0.05x0.02x3.0
$C_6H_5COCH_3$	TTT	ClO_4	1.5	2.13	0.05x0.02x2.0
$C_6H_5NO_2$	TTT	ClO_4	1.2-1.5	2.13	0.05x0.02x3.0
C_6H_6	TTT	ClO_4	>>10	-	none
$C_6H_5CH_3$	TTT	ClO_4	>>10	-	none
o-$C_6H_4Cl_2$	TTT	BF_4	2.0	0.95	0.15x0.08x2.7
o-$C_6H_4Cl_2$	TTT	PF_6	1.6	0.95	0.05x0.02x3.7
$C_6H_5OCH_3$	TMTTF	BF_4	4.5	1.0	1.0x0.50x16.0
$C_6H_5OCH_3$	TMTTF	Br	5.0	1.0	powder
$C_6H_5OCH_3$	TMTTF	IO_4	4.0	1.0	none
CH_2Cl-$CHCl_2$	TMTTF	BF_4	1.5	1.0	none
C_2H_5OH	TMTTF	BF_4	1.25	1.0	0.10x0.08x4.0
CH_3CN	TMTTF	BF_4	2.25	1.0	none
CH_2Cl-$CHCl_2$	TMTSF	ClO_4	1.6	1.9	1.2x0.3x12.0
C_6H_5Cl	HMTTF	BF_4	6.0	1.0	none
C_6H_5Cl	HMTTF	PF_6	4.3	1.0	none
C_6H_5Cl	HMTTF	I_3	0.7	1.0	none
C_6H_5Cl	HMTTF	ClO_4	3.9	1.0	none

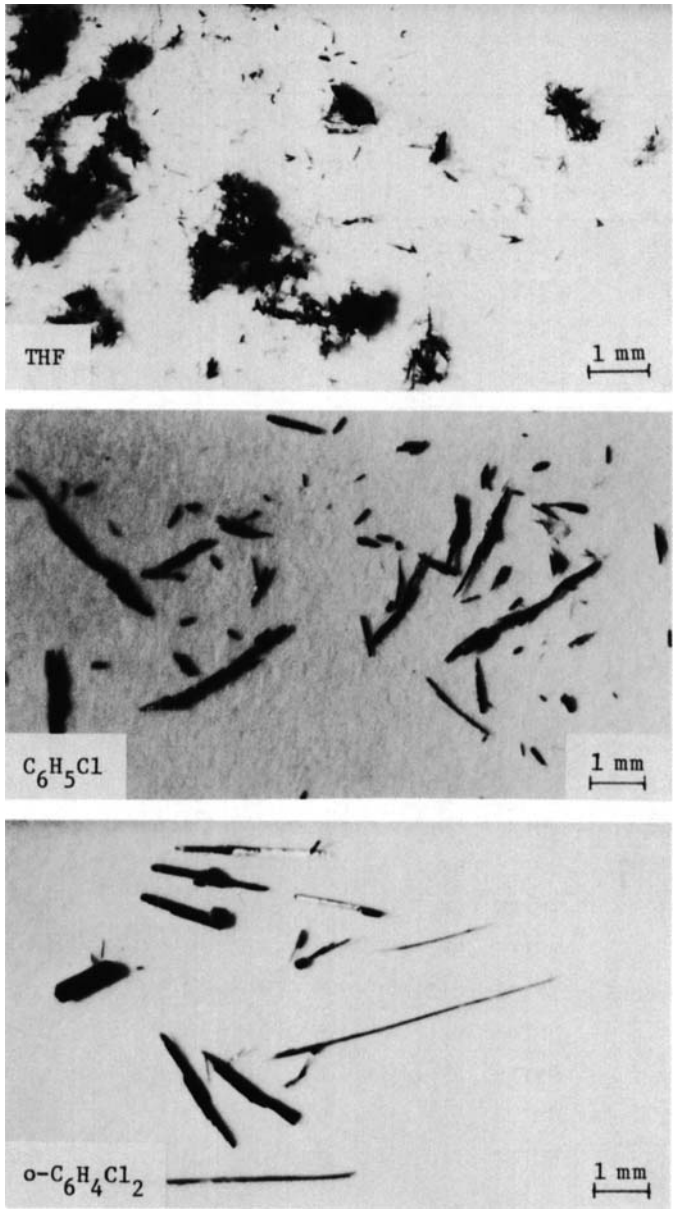

FIGURE 2. Pictures of crystals obtained from TTT and ClO_4^- anions in various organic solvents.

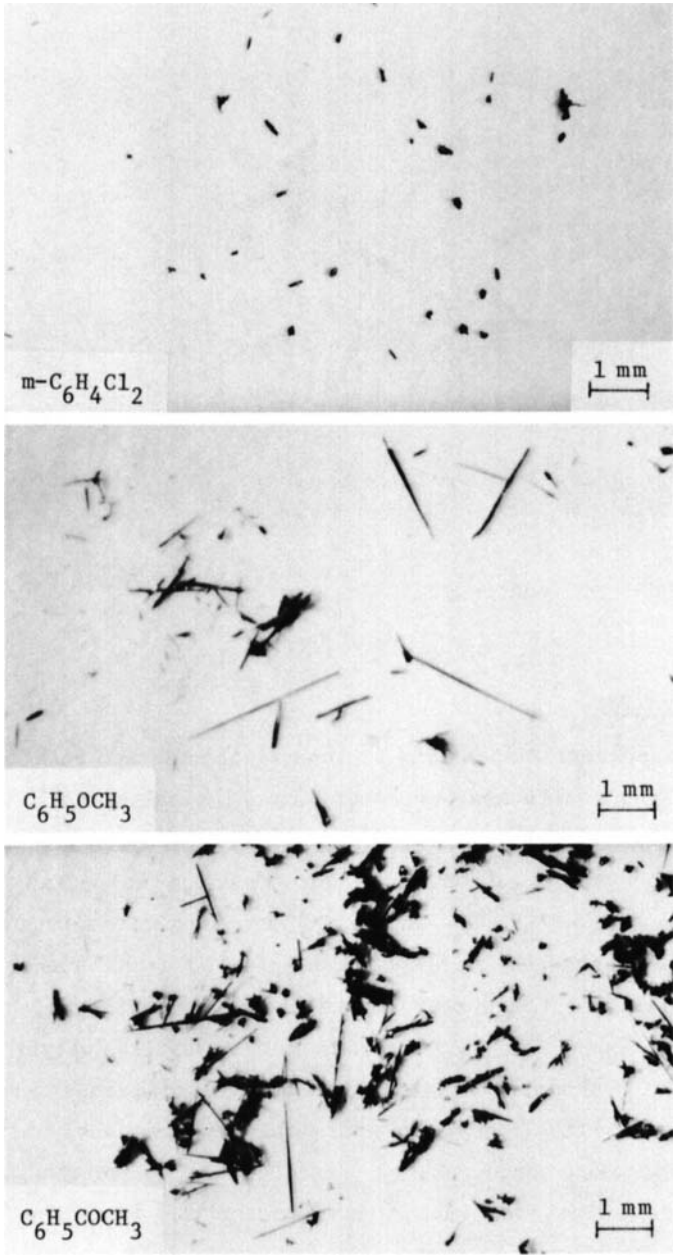

FIGURE 2. (continued)

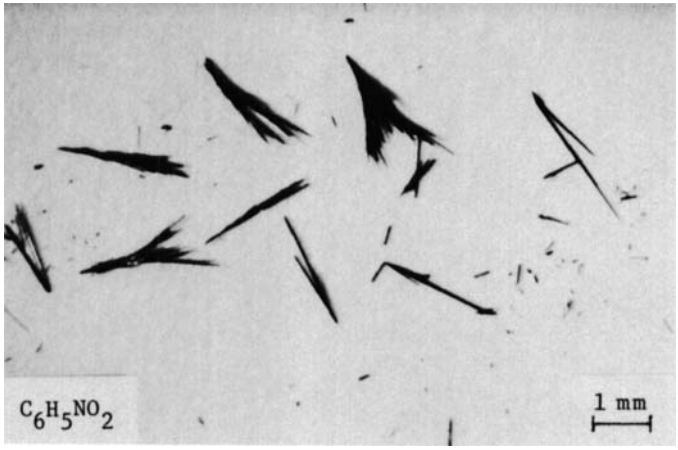

FIGURE 2. (continued)

DISCUSSIONS

Polar solvents such as acetone, ethanol and acetonitril dissolved easily most tetrabutylammonium salts and other low molecular weight donors, and were suitable for their electrocrystallization, but not for high molecular weight donors like HMTTF, TTT and BEDT-TTF. Aromatic solvents such as chlorobenzene, dichlorobenzene, anisole and nitrobenzene were suitable for electrocrystallization of high molecular weight donors as well as for low molecular weight ones. Most halo-aromatic solvents and most halo-alkanes were also good solvents. They can presumably change chemically Bu_3N or Bu_2N-NBu_2 produced by electrolytic reduction on the surface of cathode into a new electrolyte according to the reactions presented previously:[4]

$$2Bu_4N^+ + e^- \rightarrow 2Bu_4N\cdot \rightarrow 2Bu_3N + Bu\text{-}Bu$$
$$\text{or} \quad \rightarrow Bu_2N\text{-}NBu_2 + 2Bu\text{-}Bu \qquad (1)$$

further,

$$Bu_3N + R\text{-}Cl(\text{solvent}) \rightarrow Bu_3RN^+Cl^{-*}$$
$$Bu_2N\text{-}NBu_2 + R\text{-}Cl \rightarrow Bu_2RN^+\text{-}NBu_2Cl^{-*} \qquad (2)$$

where * indicates newly produced electrolyte.

Benzene, toluene and other aromatic hydrocarbons can dissolve numerous tetrabutylammonium salts as a general rule, but the sulutions prepared by the use of such solvents don't carry electric current; therefore the efficiency of the crystal growth is very low in such nonpolar solvents. In this case, it may be expected that the electrolyte exists in a molecular state, i.e. a contact ion-pair in the solvent without any electrolytic dissociation. HMTTF is a little soluble in nitrobenzene, chlorobenzene and tetrahydrofuran, but almost insoluble in other organic solvents. However, many of HMTTF complexes synthesized from several anions(for example, ClO_4^-, PF_6^-, and BF_4^-) were more soluble in the most organic solvents without alkanes and aromatic hydrocarbones. In this case, it was very difficult to obtain the single crystal of the HMTTF complexes by electrocrystallization, which deserves evaluation of its physical properties. BEDT-TTF is soluble in chlorobenzene, but BEDT-TTF complexes obtained from anions of ClO_4^- and BF_4^- were insoluble in it. From such solvents, we could obtain their complexes only in the form of powders or aggregate of microcrystals. It is very interesting that we could detect only the β-form from many crystals of $(BEDT\text{-}TTF)_2I_3$ which were prepared from BEDT-TTF and Bu_4NI_3 in chlorobenzene.

There may be some relation between the structure of the obtained crystal and the solvent used for crystal growth. We will report about this relation elsewhere.

CONCLUSION

We conclude that suitable solvent for crystal growth of organic charge transfer complex by electrocrystallization has ability to dissolve easily its donors and supporting electrolyte, but to dissolve slightly the produced complex, from our results which has been studied about crystal growth of organic metals by this time.

REFERENCES

1. H. Anzai: J. Cryst. Growth, 47, 733 (1979)
2. T. Ishiguro, H. Sumi, S. Kagoshima, K. Kajimura and H. Anzai: J. Phys. Soc. Japan, 48, 456 (1980)
3. S. Kagoshima, J. P. Pouget and H. Anzai: J. Phys. Soc. Japan: 52, 1629 (1983)
4. H. Anzai, T. Moriya, K. Nozaki, T. Ukachi and G. Saito: J. Physique Colloque C3, 44, C3-1195 (1983)