This Week's Citation Classic

CC/NUMBER 39
SEPTEMBER 27, 1982

Melby L R, Harder R J, Hertler W R, Mahler W, Benson R E & Mochel W E. Substituted quinodimethans. II. Anion-radical derivatives and complexes of 7,7,8,8-tetracyanoquinodimethan. *J. Amer. Chem. Soc.* 84:3374-87, 1962. [Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, DE]

This paper describes the synthesis and electrical properties of salts of the anion-radical of 7,7,8,8-tetracyanoquinodimethan (TCNQ), a new class of organic semiconductor which at the time included the most highly electrically conducting organic materials known. Moreover, their conductivities and electron spin resonance spectra were highly anisotropic with respect to the crystal axis. Subsequent studies at Du Pont and other laboratories worldwide led to discoveries of organic 'metals,' so called because of their unusual metal-like electrical properties. [The *SCI*® indicates that this paper has been cited in over 520 publications since 1962.]

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June 28, 1982

"Our discovery of the anion-radical salts of 7,7,8,8-tetracyanoquinodimethan (TCNQ) began an era of intense interest in the physics of organic solids. Along with that the disciplines of organic chemistry and physics showed a remarkably productive interplay in quest of new materials having unconventional electronic properties.

"Before I describe our work I must acknowledge that of William D. Phillips whose name does not appear on our paper. He has long since left our laboratories but at the time it was the cooperation between Phillips and me that originally stimulated this work.

"In 1959, much of the work in our department dealt with the chemistry of polycyano compounds and I was looking for practical uses for such compounds. My project was beginning to fade so as a side issue I made some π-complexes from conventional π-acids and π-bases because Phillips was interested in examining their ESR spectra. Among those was that from chloranil and diaminodurene (CA/DAD), and Phillips asked one of our physicists, Glen Kepler, to measure the electrical resistivity of this material. It showed a room temperature resistivity of around 3×10^3 ohm cm., the lowest value reported for an organic compound at that time, and the temperature dependence was characteristic of semiconduction. I proceeded to make a variety of complexes from the π-acid TCNQ which had come from the cyanocarbon research in our department. These showed characteristics similar to CA/DAD and this quickened our interest because TCNQ was our proprietary material. Bob Harder, Wally Hertler, and Walter Mahler were also assigned to expand our synthetic work.

"Hertler quickly discovered a crystalline derivative of TCNQ and triethylamine which had a needle axis resistivity of 0.5 ohm cm.! Moreover, the resistivity was highly anisotropic with respect to the two other crystal axes. With help from our physical people, Hertler and Harder showed that it represented a new class of complex incorporating one cation, one TCNQ anion-radical, and a neutral molecule of TCNQ, which we abbreviate as $M^+(TCNQ)_2^-$, and which we call complex ion-radical salts. From that basis we were able to synthesize a host of organic semiconductors.

"To that point our methods had generated the TCNQ anion-radical in the presence of neutral TCNQ, and the propensity for complex salts to form under these conditions frustrated our attempts to make the simple salts $M^+ TCNQ^-$. We wanted these very badly for comparison with the complex salts. The key was provided by Mahler who came up with the lithium salt $Li^+ TCNQ^-$ which was soluble enough in organic media to allow us to prepare $TCNQ^-$ simple salts by metathesis with quaternary ammonium and other organic or inorganic salts. Using this technique I prepared N-methylphenazinium $TCNQ^-$ which proved to be the first organic compound to show metallic conductivity rather than semiconduction.[1,2]

"Subsequent work in other laboratories branched from this to other derivatives of TCNQ which show even higher metallic conductivity[2,3] and to other materials which, although chemically unlike those derivatives, behave like organic metals. So continues the search for new materials, new properties, and new uses."

1. **Melby L R.** Salts derived from the TCNQ anion-radical and benzologues of quaternary pyrazinium cations. *Can. J. Chem.* 43:1448-53, 1965.
2. **Garito A F & Heeger A J.** The design and synthesis of organic metals. *Account. Chem. Res.* 7:232-40, 1975.
3. **Ferraris J P, Walatka V V & Perlstein J H.** Electron transfer in a new highly conducting donor-acceptor complex. *J. Amer. Chem. Soc.* 95:948-9, 1975.