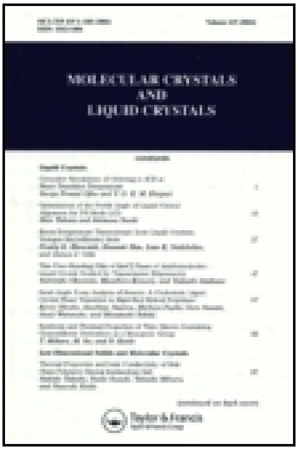

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Organic Semiconductors and Conductors: Start of Research in Japan

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Organic Semiconductors and Conductors: Start of Research in Japan

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I report why and how I became engaged in the study of organic semiconductors. My first step (1947) in the investigation of organic semiconductors was the measurement of electrical resistance of powdered graphite and carbon materials. Through this observation I accepted the property that carbon particles certainly conduct electric current. I noticed that functional groups bound to the edges of polycyclics in graphite do not cause swelling. I hit upon an idea that polycyclic aromatic compounds with molecular structures similar to fragments of graphite might be electrically conductive. Then, I started measuring the electrical resistance of violanthrone and hence found semiconductive behavior in organic solids (1954).

Further I present my encounter with charge-transfer type organic semiconductors.

Keywords: charge-transfer type organic semiconductors; organic semiconductors

1. INTRODUCTION

In the 1940s, dyestuffs [1] such as cyanine dyes, phthalocyanines [2] and polycyclic aromatic compounds [3] were major objects of study and the quantitative investigation of electrical conductivity of organic compounds was started (Fig. 1). In the following section, we present why and how we were engaged in the study of single component "organic semiconductors".

There is another significant branch in organic semiconductors, i.e., a group of charge-transfer type organic semiconductors. H. Akamatu, Y. Matsunaga and myself reported these works of charge-transfer type organic semiconductors in 1954: the historical background of this work

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Researchers	A. T. Vartanyan	D. D. Eley	H. Akamatu H. Inokuchi
Organic Materials	Cyanine Dyestuffs	Phthalocyanine	Violanthrone
Standpoint	Photo-Sensitization	Biochemical	π-electron of aromatics
Picture	about 1960 	1955 	1965 

FIGURE 1 Discoveries of electrical conduction in organic solids.

was completely different from the single component group as described in Section 2. We present a historical survey of the discovery of charge-transfer type organic semiconductors (binary type) in Section 3.

2. THE ENCOUNTER WITH ORGANIC SEMICONDUCTORS

All research works have tradition and succession, and they are further developed by the successors. My graduate research was carried out in Jitsusaburo Samejima's laboratory, in the Chemistry Department of the University of Tokyo. The photograph shown in Figure 2 was taken in 1920, and displays at the back a helium-liquefier installed at Leiden University in the Netherlands. A large amount of active charcoal was packed in the column, i.e., an adsorbing tower, located at the central part of the liquefier in order to remove moisture from gaseous helium for liquefaction as shown in Figure 2.

Samejima returned to Japan, planning to embark on research in low-temperature chemistry, but the purchase of a helium-liquefier became extremely difficult due to the disastrous aftermath of the earthquake that struck the Kanto area of Japan in 1923. Therefore he shifted the object of his study to the field of colloid chemistry, starting research on active charcoal.

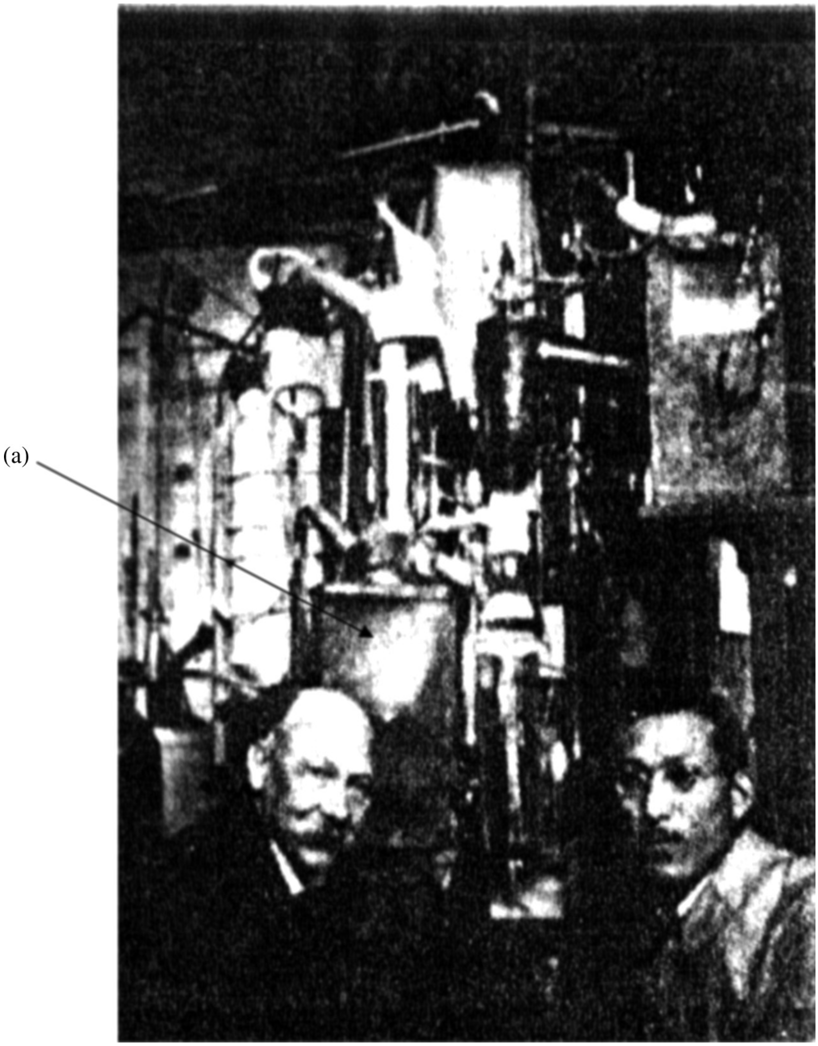


FIGURE 2 H. Kamerlingh Onnes (left) and J. Samejima (right). (a) is a large column of active charcoal.

The measurement of electrical resistance of carbon materials, which was a sort of solid colloid, was the theme of the graduate project given to me by Samejima and Hideo Akamatu (Fig. 1) in 1947. I believe this was my first step towards investigating organic semiconductors and therefore the column of active charcoal shown in the photograph (Fig. 2) could be referred to as the origin of my lifelong study.

The damage from air raids was slight in the Hongo district, only a few university buildings having suffered from fires. Nevertheless, circumstances of experimental researches were quite inadequate; the power supply was insufficient, city gas was provided only for certain hours and chemicals were scarce. However, I had good friends who encouraged me, and we were keen on studying issues in other scientific fields. For example, someone proposed to read a book on solid state physics, and in fact we read and studied Seitz's *The Modern Theory of Solids*. The atmosphere of the laboratory was free and energetic, and besides, we had the benefit of time for thinking, when things were moving on rather slowly.

Subsequently my study of carbon materials shifted to organic compounds. It was known that carbon and graphite were composed of hexagonal networks made of condensed polycyclics as described above. Each carbon atom located at the corner of the hexagons in the networks possessed a π-electron that brought about electrical conductivity in the entire network. It was, however, sometime later that I noticed a big error in a diagram of graphite shown in a textbook. The error occurred at the edge of a gigantic molecular plane, which terminated at the edge with dangling bonds, i.e., so-called free bonds of high reactivity, so that such a molecular plane of graphite, as depicted in Figure 3, did not exist. In reality, the edge of graphite is terminated by various kinds of functional groups as shown in Figure 4. The bonding of functional groups was realized through the following two experiments.

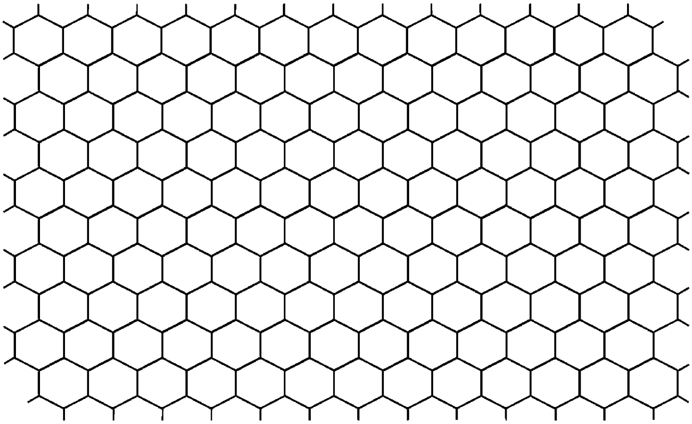


FIGURE 3 A single gigantic molecular sheet of graphite.

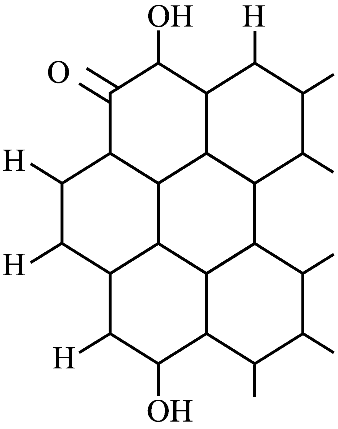


FIGURE 4 Structure of graphite (molecular edge).

Carbon materials are classified into carbon blacks, acetylene blacks, active charcoal, bituminous coal and graphite, and the subject of my experiment was concerned with measuring their electrical resistance. Reproducible values were hard to obtain from the initial trials with packing carbon powder into an ebonite cylinder and measuring the electrical resistance. However, when the experiments were repeated many times, the values began to converge to a definite one. Finally, I could accept the conclusion that carbon particles certainly conducted electric current. However, there still remained a question as to how electrons could leap from particle to particle.

One result obtained from a simple experiment greatly influenced my speculations about electrical conduction in carbon powders. The experiment was carried out with copper powders familiar in chemistry laboratories. They were the bright shining copper powders used as a reducing agent. Since graphite powders were highly conductive, it could be assumed that the clean copper powders would show a high value, but the value of electrical conduction was feeble. I noticed that such a phenomenon as a jump of an electron from a copper particle to another did not occur, because an oxide film covering the particle obstructed the jump.

Concerning the edge of polycyclics, I noticed that functional groups bound to edges of these units in graphite did not swell. Here I hit upon an idea that polycyclic aromatic compounds with molecular structures similar to pieces of graphite might likewise be electrically conductive.

Figure 5 shows an apparatus for measuring the electrical conductivity of carbon powders, manufactured by Takeo Ikeda in the machine

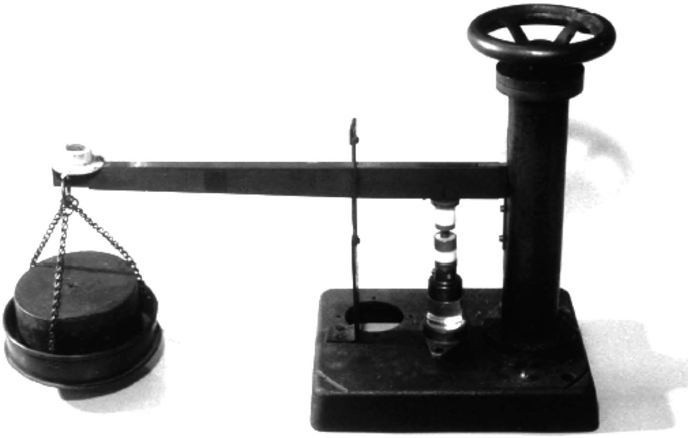


FIGURE 5 An apparatus for compressing powders (for an electrical conductivity measurement).

shop at the Institute for Physical and Chemical Research (1947). It can compress a powder sample packed in a tube from the top up to a pressure of 150 kg cm^{-2}. I have a lot of memories related to this device, and it is still working for a physical chemistry laboratory class in a university. It is mentioned here because it was the starting point for the study culminating in an experiment on the electrical conductivity of organic materials under high pressures, which will be related below. I believe this apparatus contributed much to establishing the concept of organic semiconductors.

The electrical resistance of carbon powders was measured by changing the applied pressure. It was supposed that a jump of an electron from one graphite molecule to an adjacent one occurred through a functional group similar to one found on an organic compound, because the edges of graphite were not covered with thick substitute films. It was already known that graphite was also conductive along the c-axis, so that the experiment was repeated in consideration of that fact, too.

At that time violanthrone was being studied in our laboratory by Akamatu and Kazuo Nagamatsu as a structural model of carbon blacks [4]. Thereupon I decided to measure the electrical resistance of violanthrone, which was a sort of condensed polycyclic aromatic molecule possessing a molecular structure similar to graphite, though organic compounds containing fully saturated bonds had been regarded as electrical insulators. This is an image of organic semiconductors that has long been entertained in my mind, though it may seem very simple.

Violanthrone is a molecule with nine benzene rings. The value of the electric current that would pass through such materials was hard to estimate, and it caused a serious problem. There was no clue how to choose and settle the method of measurement. It was extremely difficult to observe a weak current in those days. In a strenuous search for a breakthrough, I happened to think of an electrometer called a "quadrant electrometer" which had long been kept in our laboratory, and with that apparatus started to measure the electrical resistance of organic compounds.

The purity of samples was another crucial problem. The commercially available dyestuff, violanthrone, contained various kinds of impurities, which had to be removed. Thus a very hard task of purification started. For half a year, the measurements were repeated day by day on samples purified by dissolution into concentrated sulfuric acid followed by sublimation *in vacuo*. Through repetition, a real signal came to be distinguished from the noise, and with an increase in purity, the true signal could be finally detected by means of the "lamp and scale" of the electrometer. From these results, it was confirmed that even organic materials were undoubtedly electrically conductive, the value of electric current being 10^{-12}–10^{-13} A for an applied voltage of 1 V.

At that point it seemed to me clear that organic materials would also be able to pass electric current. The first paper on electrically conductive organic materials was prepared together with Akamatu, and submitted to an American journal [3]. Even after the paper was accepted, I could not but feel uneasy about our conclusion that organic materials intrinsically conduct electric current. Colleagues in the laboratory positively supported us, but others were not always favorable and criticized with such comments that the current might have passed along a surface of the cylindrical container, or it might be something else, not inherent to the materials. Various kinds of experiments were performed to meet these criticisms, which brought conviction for the most part, but some concern still remained in our final result.

Several good results were obtained in the years 1949–1954. One of them was the determination of the electrical resistivity for violanthrone to be *ca.* $10^{12}\,\Omega\,\mathrm{cm}$, and therefore, an electric current of 10^{-12} A would pass through it for an applied voltage of 1 V. It was known that such a feeble current could be measured by an electrometer capable of amplification. Fortunately I was able to learn a technique for measuring high resistances under the guidance of Hideya Gamou and Goro Kuwabara of the Physics Department, Faculty of Science. Further, Saburo Izawa of Toshiba, who was an acquaintance of my father's, presented me with a vacuum tube UX-54 for high-resistance measurements. I remember how delighted I was when I visited the Matsuda Research Laboratory of Toshiba in Kawasaki, which was partially destroyed by aerial bombing, and brought back the tube, wrapping it with fluffy silk threads for protection.

Another course of research a chemist should pursue, it seemed to me, was to measure electrical resistance for a number of polycyclic aromatic compounds, in parallel with the determination of its value. Various sorts of aromatic compounds were synthesized or separated from coal tar. This type of work might be routine for a chemist, but it was certainly what should be done. Japanese scientists had maintained a tradition of producing remarkable results in research on polycyclic aromatic compounds. Lots of polycyclic aromatic compounds were prepared in cooperation with Takashi Handa and Junji Aoki in Toshio Maki's and Yoshio Nagai's laboratories of the Applied Chemistry Department, Faculty of Engineering, the University of Tokyo. Purifying them, which was exceedingly difficult, was my job and most of my time for experiment was spent on this work. The fact that the

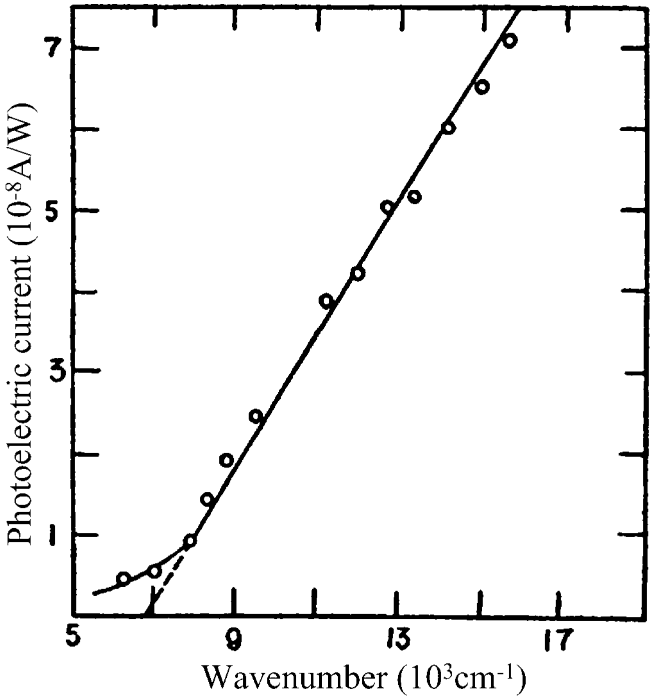
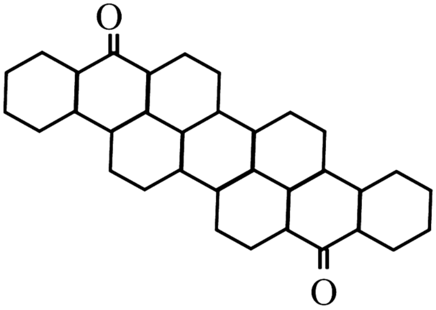


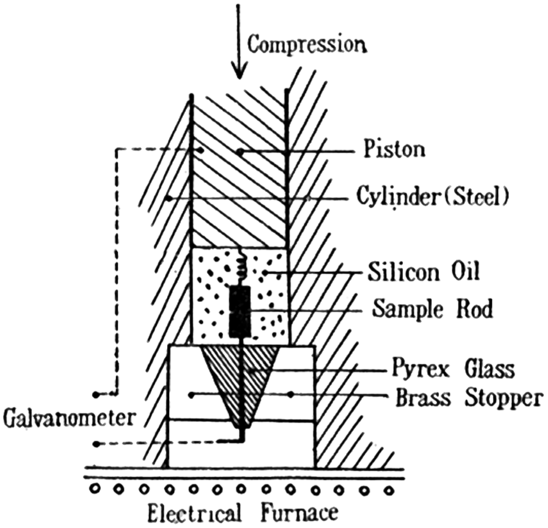
FIGURE 6 "Organic semiconductors" (1954) [6], and the spectral response of photoconductivity for a violanthrone film [5].

aim was clear might have encouraged my concentration and I worked many hours, exerting my youthful energy on the task.

The greatest outcome was success in measuring photoconductivity in organic materials. It is a special feature of organic materials that they are composed of independent molecules that easily form thin films upon sublimation *in vacuo*, and indeed the present article is based on this fact. The measurement of photoconduction in violanthrone (Fig. 6) was successful when a thin film was used [5,6], and



(a)



(b)

FIGURE 7 (a) Isoviolanthrone and (b) a diagram of a compression apparatus [7].

TABLE 1 Semiconductivity of Isoviolanthrone with Compression (P) [8]

P (kg/cm^2)	$\rho_{15^\circ\mathrm{C}}$ (Ω cm)	ΔE (eV)^a
3×10^2	5×10^9	0.75
4.2×10^3	8.4×10^7	0.74
6.3×10^3	2.6×10^7	0.69
8.4×10^3	1.2×10^7	0.68

$^a\rho = \rho_0 \exp(\Delta E/2kT)$

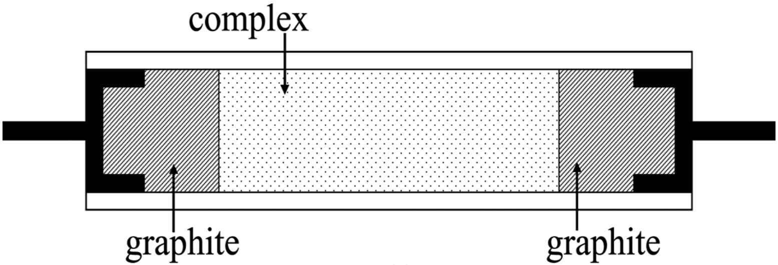
the result confirmed the concept that this kind of organic material was electrically conductive. I named them "Organic Semiconductors" in 1954 in the paper that appeared in *Bull. Chem. Soc. Jpn.* [6].

Seven years passed since I first noticed the possibility of electrical conduction in organic materials. The long time needed to confirm the concept, however, had not mattered much, since, I suppose, other things also progressed slowly.

Another experimental success was the measurement of the effect of pressure on isoviolanthrone (Fig. 7). As described already, powders of carbons or organic material packed in a cylinder under the pressure of 80 kg cm^{-2} by means of the apparatus mentioned above gave a nearly constant value of electrical resistance, which seemed to imply the situation that the powders were always packed uniformly. Then, without studying the essential part of a high-pressure experiment, I tried to perform an experiment under much higher pressures. Under such conditions, the electrical resistance was found to reduce to the easily measurable value of $10^7\,\Omega$ cm (Table 1), and moreover, the resistance reversibly returned to the original one when the applied pressure was removed [7]. These results brought a conception that intermolecular distances in organic crystals might shrink under high pressures. I was extremely pleased with this discovery. The equipment used for applying pressure was made from a piston for a scooter given by Tatsuhisa Fukushima of Fuji Heavy Industries (Fig. 7).

3. CHARGE TRANSFER TYPE ORGANIC SEMICONDUCTORS

There is another significant branch of organic semiconductors, i.e., a group of charge-transfer type. The binary organic semiconductors started from a historical background completely different from that of single-component ones. In the 1930s, Eric Clar in Germany and Alois Zinke in Austria were engaged in synthesizing polycyclic aromatic compounds and there was a dispute between these two well-known chemists about the composition of a very dark blackish brown addition compound formed by reaction between perylene ($C_{20}H_{12}$) and bromine. Clar prepared it by dropping liquid bromine into perylene dissolved in benzene, while Zinke formed it by allowing bromine vapor to be absorbed by perylene crystalline powders. Yoshio Matsunaga [Fig. 8 (b)] was interested in the compounds, and we decided to synthesize it by Zinke's method. It was the time when Matsunaga was studying magnetic properties of organic materials under Akamatu's guidance, and it began to be known that radicals showed paramagnetism, whereas others generally showed diamagnetism. The addition compound showed an extraordinary large paramagnetism and quite dark color, so that it was presumed that the solid of the compound might possess electrons moving freely in it. The measurement of its electrical conduction resulted in the recognition



(a)

(b)

FIGURE 8 (a) A specimen cell for a conductivity measurement of perylene-Br_2 [8] and (b) Y. Matsunaga (photo taken in 1960).

TABLE 2 Charge Transfer Organic Semiconductors (Halogen-Doping) [9]

Complex (composition)	ρ (Ω cm)	ΔE (eV)
Perylene-Bromine (1:4.4)	7.8	0.13
Pyranthrene-Bromine (1:3.3)	220	0.20
Violanthrene-Bromine (1:4.5)	66	0.20
Violanthrene-Iodine (1:4.0)	45	0.15

of charge transfer complexes as a further type of organic semiconductor. This research was performed in the years 1952–1953, and was favored by unexpected good fortune.

When a voltage was applied to a sample in an attempt to measure its resistance, an electric current passed for a moment and then diminished at once, due to an influence of bromine included in the sample. The electrodes on the sample were destroyed by reaction with bromine. At that time, graphite intercalation compounds were being studied in Akamatu's laboratory by mixing bromine with graphite to insert bromine molecules into the interlayer spaces of graphite. Then it dawned on me that an excess amount of bromine in the sample could be absorbed by graphite, and accordingly graphite powders were inserted between the electrode and the sample on both sides [Fig. 8(a)]. The electric current was established by this means, and measured successfully. In fact, an electric current much larger than our expectation passed through this system. After repeating the experiments, we came to the conclusion that the compounds were quite highly conductive.

The next question was concerned with the type of charge carrier, whether it was an ion or electron. Since the method of deciding the type of charge carrier had already been established in the field of physics, we repeated the confirmation work by the same method, and proved it to be electronic. All the results were published as a rapid communication [8]. (Table 2 [9]) This is what is now called halogen-doping and enormous numbers of research results were achieved by means of halogen-doping.

TABLE 3 Charge Transfer Organic Semicoductors Formed by Reaction Between Organic Compounds [10]

		Donor (*N*,*N*-dimethylaniline)		
Acceptor		Chloranil	Bromanil	Iodanil
ρ (Ω cm)	a.c.	5.0×10^7	9.0×10^7	3.0×10^7
	d.c.	8.0×10^8	1.5×10^9	1.7×10^8

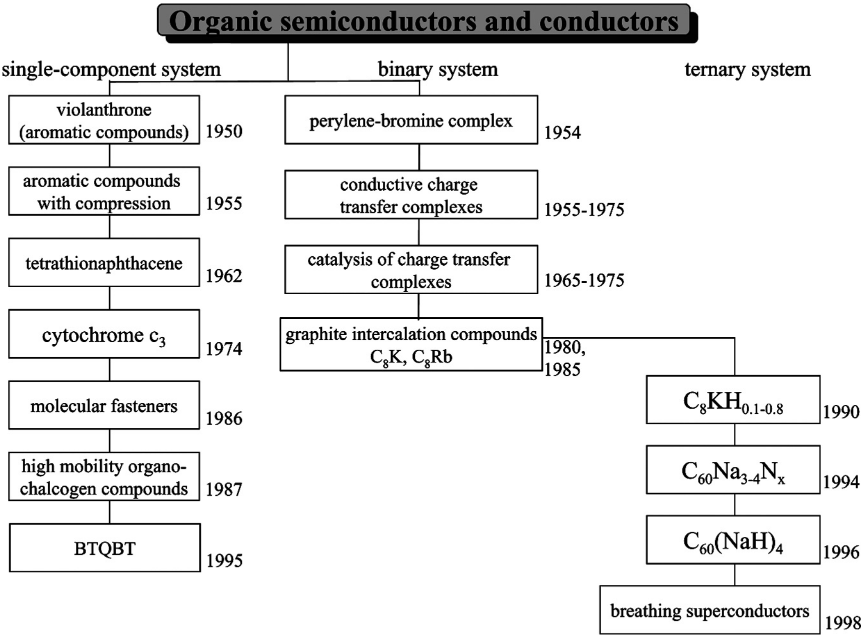


FIGURE 9 The flow chart of research progress on organic semiconductors and conductors in our group.

We prepared semiconductors by reaction between organic compounds under the guidance of Daniel D Eley (Table 3). I think this was the time when organic semiconductors composed of only organic components were established [10]. Succeeding rapid developments in this field have been reported in numerous papers, but I will mention two of them briefly. One is a synthesis of tetracyano-p-quinodimethane (TCNQ) by the chemists of Du Pont [11], and the other is that of tetrathiafulvalene (TTF) by F. Wudl, *et al.* [12]. A complex prepared by mixing these two compounds contributed to the discovery of metallic conductivity in organic materials.

The discovery of an organic superconductor made by D. Jérome, *et al.* in France in 1980 resulted from a great evolution of a TTF–TCNQ binary system through an effective use of high pressure [13].

4. CONCLUDING REMARKS

As a concluding remark, I refer to ternary organic semiconductors, shown in the flowchart of research process of organic semiconductors conductors of our group (Fig. 9). Ternary organic semiconductors have been studied, in order to develop new materials. The origin of this endeavour is found in the graphite intercalation compounds mentioned above. Kenichi Imaeda and I happened to find a very interesting phenomenon in a ternary system. When hydrogen was used as one of three components, hydrogen was not only simply accommodated in the system, but it also contributed to the electrical conductivity. This phenomenon is very fascinating to one who studies materials. Hydrogen, being a gaseous material, can be easily pumped out from the system, which changes its properties, and when hydrogen is absorbed into the system, it returns to the original one. This system was named a "Breathing superconductor", because this ternary system was an organic superconductor [14].

Fifty years have passed since I kept watching day after day at a fan-shaped light spot of a quadrant electrometer shifting within 1 mm or so long on a scale bar. It is a great pleasure for a scientist like me, who has concentrated on experiment, to have witnessed the situation that the electrical conductivity of organic materials has been accepted without question.

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