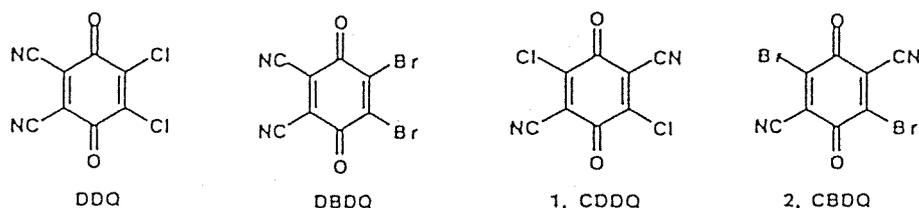


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学位論文題目	Synthesis and Properties of Centrosymmetric DDQ Analogues and Their Charge-Transfer Complexes
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論文内容の要旨

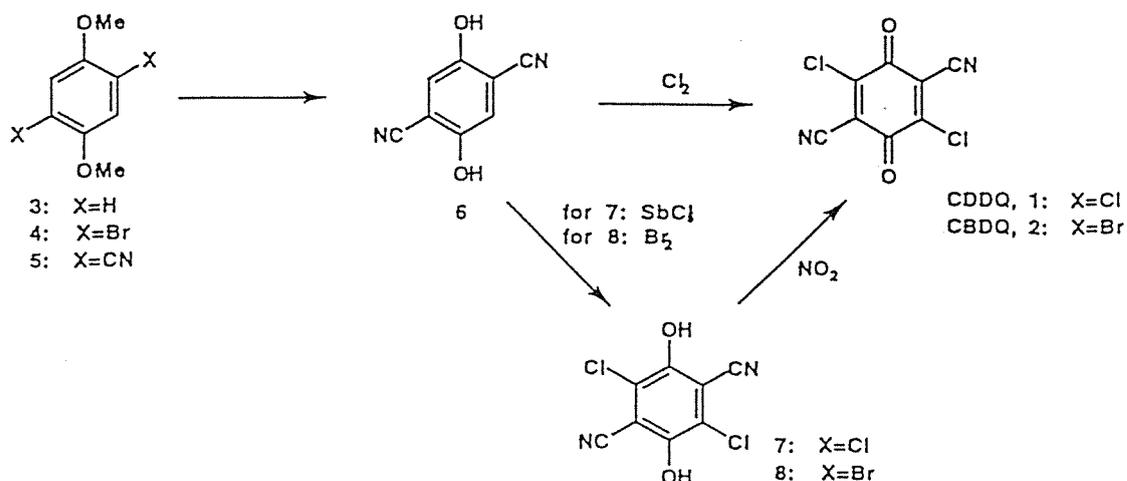
Interdisciplinary cooperation between synthetic chemistry, physical chemistry, and the solid state physics has opened a new field of science which focuses on the development and study of molecular materials having interesting electrical, magnetic and optical properties in the solid state. Since the solid state properties of the molecular materials depend on the molecular symmetry or spatial arrangements, it is interesting to study and design new molecular materials with centrosymmetric nature.

An important electron as well as hydride and proton acceptor in the solid state chemistry and physics is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) whose molecular symmetry is C_{2v} . The positional isomer of centrosymmetric DDQ, 2,5-dichloro-3,6-dicyano-1,4-benzoquinone (1, CDDQ), possesses C_{2h} molecular symmetry. Therefore, we studied the basic properties of CDDQ, such as a convenient synthetic procedure, molecular properties, crystal structure, and the physical properties of the charge-transfer complexes with variety of donors in order to clarify the differences of solid state properties compared with DDQ and to obtain new molecular materials. In addition, a centrosymmetric bromo derivative, 2,5-dibromo-3,6-dicyano-1,4-benzoquinone (2, CBDQ), was also synthesized and studies the basic properties.

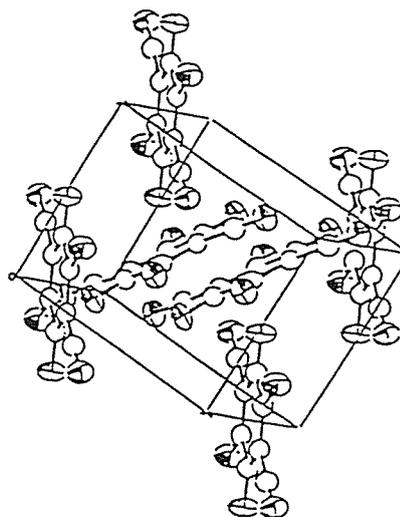


Two methods were described by two groups for preparing DDQ analogs with centrosymmetry. The first synthetic method was started from 1,4-benzohydroquinone and the introduction of chlorine or bromine atom at the earlier step and then transformation of functional groups. They suppose it is not easy to prepare a large amount of both quinones because of their long steps of synthesis even if the chemical yield of each reaction is pretty high. While second one for the synthesis of 1 is more convenient synthetic route using the four steps procedures; but they did not described the other centrosymmetric DDQs, especially 2, CBDQ. According to this short steps method, they have studied the syntheses of 1 in detail and opened an improved synthetic method of 1. Furthermore, they have also found a new synthetic procedure for 2. These synthetic procedures are reproducible on a large scale from only one precursor, 2,5-dicyano-1,4-hydroquinone 6 (scheme 1).

Scheme .1



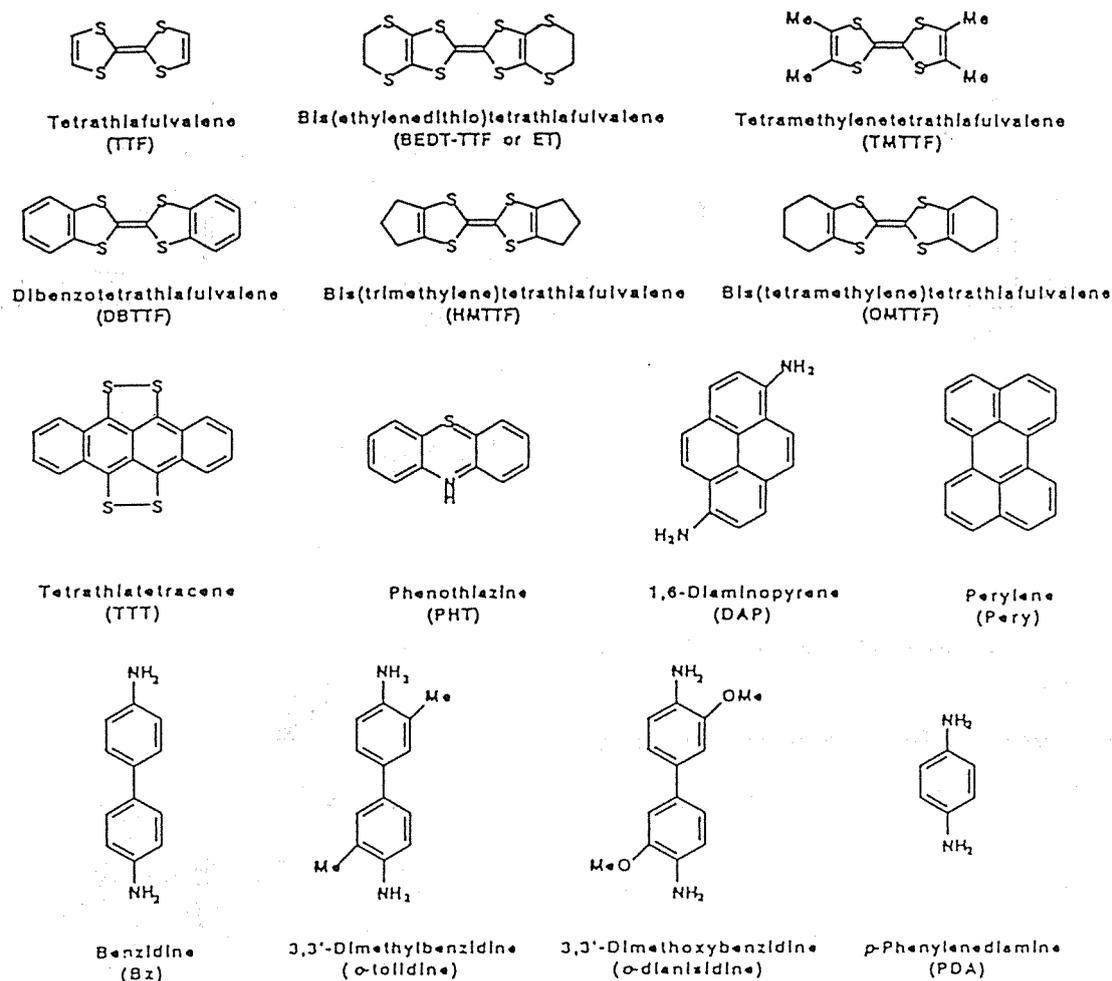
The melting point of CDDQ and CBDQ are 209 °C and 220 °C, respectively. Their appearances are light yellow needle-like crystal and they are soluble to common organic solvents. These are slowly decomposed in organic solvents containing water. The cyclic voltammetry measurements were carried out in PhCN and reveal that these compounds are good acceptors. These acceptors exhibit two pairs of reversible waves corresponding to one-electron transfer processes.



The crystal structure of CDDQ

Both half-wave potentials of 1 ($E=+0.55$ V and -0.36 V vs SCE) and 2 ($E=+0.53$ V and -0.31 V vs SCE) have comparable strength to that of DDQ ($E=+0.59$ V and -0.30 V vs SCE) and DBDQ ($E=+0.58$ V and -0.29 V vs SCE). Furthermore, they obtained a good crystal of 1, which was appropriate for X-ray crystallographic analysis, by two-times recrystallization from CH₂Cl₂ at 0 °C. The structure of 1 has turned out to be more planar confirmation than DDQ. The closer O...O interaction is 3.10 Å. All other intermolecular contacts are less than 3.6 Å. The geometry of 1 has a quinonoid geometry.

The solid-state charge-transfer complexes containing centrosymmetric DDQs (1 and 2) are hitherto unknown. They have used three types of donors (Scheme 2), for the preparation of charge-transfer complexes. They are (a) TTF-type derivatives, (b) aromatic amines and (c) aromatic hydrocarbons.



Scheme 2. Donors used to prepare centrosymmetric DDQs complexes.

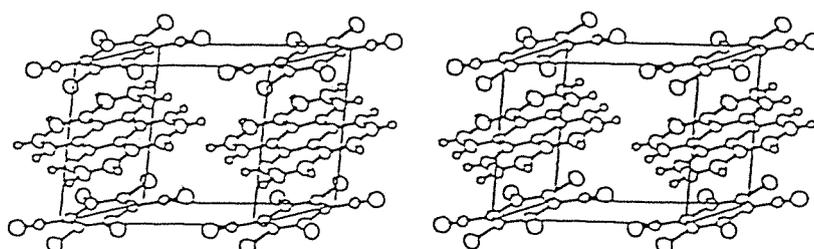
The results of the charge-transfer complexes are as follows: (a) semiconductive, black crystals were obtained with BEDT-TTF (ET), TMTTF and OMETF and black powders were obtained from TTF, DBTTF and TTT, (b) hydrogen-bonded charge-transfer complexes (based on infrared spectra) were formed from the donors, *p*-phenylenediamine, benzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine. Dark green powder were obtained from 1,6-diaminopyrene, and phenothiazine, (c) dark green crystals were obtained with perylene. A single crystal suitable for crystal structure analysis was obtained only for the perylene-CDDQ complex. All the products were studied by their optical and electrical properties.

Almost all the infrared spectra of the complexes of TTF type donors show the broad absorption ($2500-4000\text{ cm}^{-1}$) which moves to lower energies as the conductivity of the material increases. The broad bands located at around 2500 and 2850 cm^{-1} in the aromatic amine complexes constitute the pattern of the $\text{NH}\cdots\text{O}$ type hydrogen-bonded system. From the position of the $\text{C}\equiv\text{N}$ stretching frequency a neutral nature was found for the *o*-tolidine-1, phenothiazine-1

perylene-1 and perylene-2 complexes. The other CDDQ complexes were assigned to ionic (degree of charge-transfer varied from 0.57 to unity). Furthermore, the C=O frequencies were detected in the 1540-1580 cm^{-1} region, which support the anionic structures. The electronic spectra of the complexes of TTF, ET, TMTTF (dimer), DBTTF, and OMTTF with 1 and 2 reveal characteristic bands extending below 5000 cm^{-1} , leading that they have normally ionic ground state ($0.5 \leq \text{degree of CT} \leq 1$). Such low energy bands at around 6000-4000 cm^{-1} might be assigned to an intra band CT transition for a mixed valance state.

Electrical conductivities of single crystals were measured by the four-probe method, except that of OMTTF-1, perylene-1 and perylene-2 complexes. The other powder samples were measured by the two-probe method on compressed pellets. Interestingly, the ET-1, TMTTF-1 and TMTTF-2 complexes showed higher conductivity than that of DDQ. Among them, ET-1 (room temperature resistivity= 3 ohm cm) shows the highest conductivity. All the TTF type complexes show semiconducting behavior. The aromatic amines and phenothiazine complexes show typical insulating behavior. The minimum resistivity values in the range of 10^7 to 10^9 ohm cm were measured on compressed powder except that of the complexes of DAP with 1 and 2 which exhibit resistivities of the order of 10^3 ohm cm.

The crystal structure analysis of perylene-1 indicates that each molecule has a center of symmetry. The packing modes of perylene-1 consist of stacks of alternating donor and acceptor molecules, a packing motif common to the vast majority of organic charge-transfer complexes. It is of interest, therefore, to examine the relative donor-acceptor orientation in order to gain some understanding of this stacking mode in view of the orbital-symmetry.

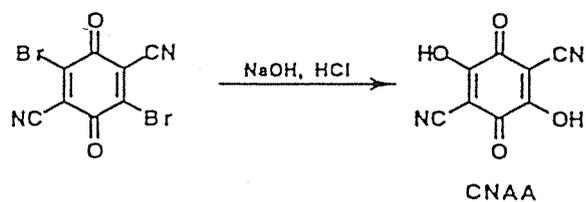


Crystal packing in perylene-CDDQ

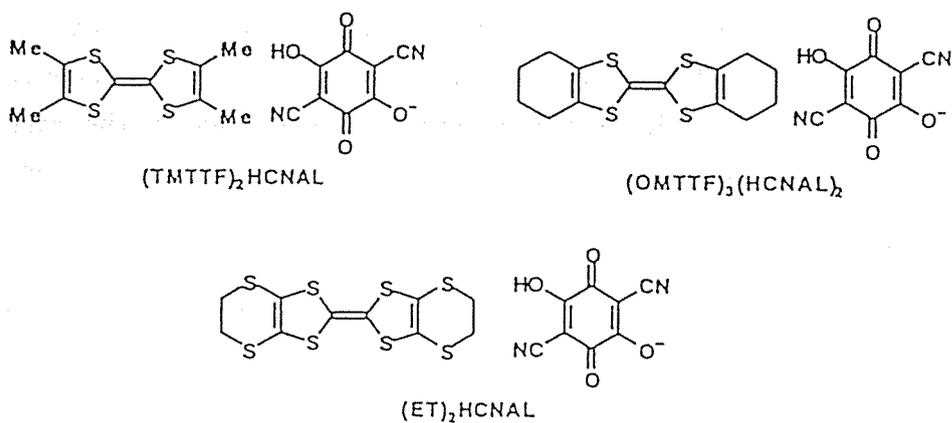
They have not obtained single crystals of CT complexes of centrosymmetric DDQs with TTF type donors so far. Interestingly, they found that the halogen atoms of centrosymmetric DDQs were substituted by the hydroxyl group and deprotonated during the crystallization processes to give a single crystal of the CT complexes of deprotonated 2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone, that is, hydrogen cyananilate (HCNAL), with TMTTF. The cyananilic

acid (CNAA) acceptor was prepared according to known procedure (Scheme3) and successfully gave the same single crystals, (TMTTF):HCNAL.

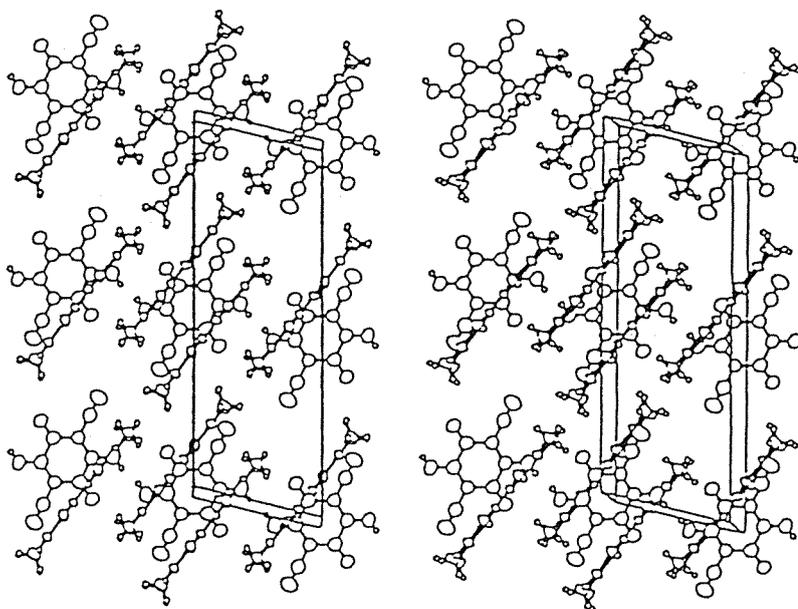
Scheme 3.



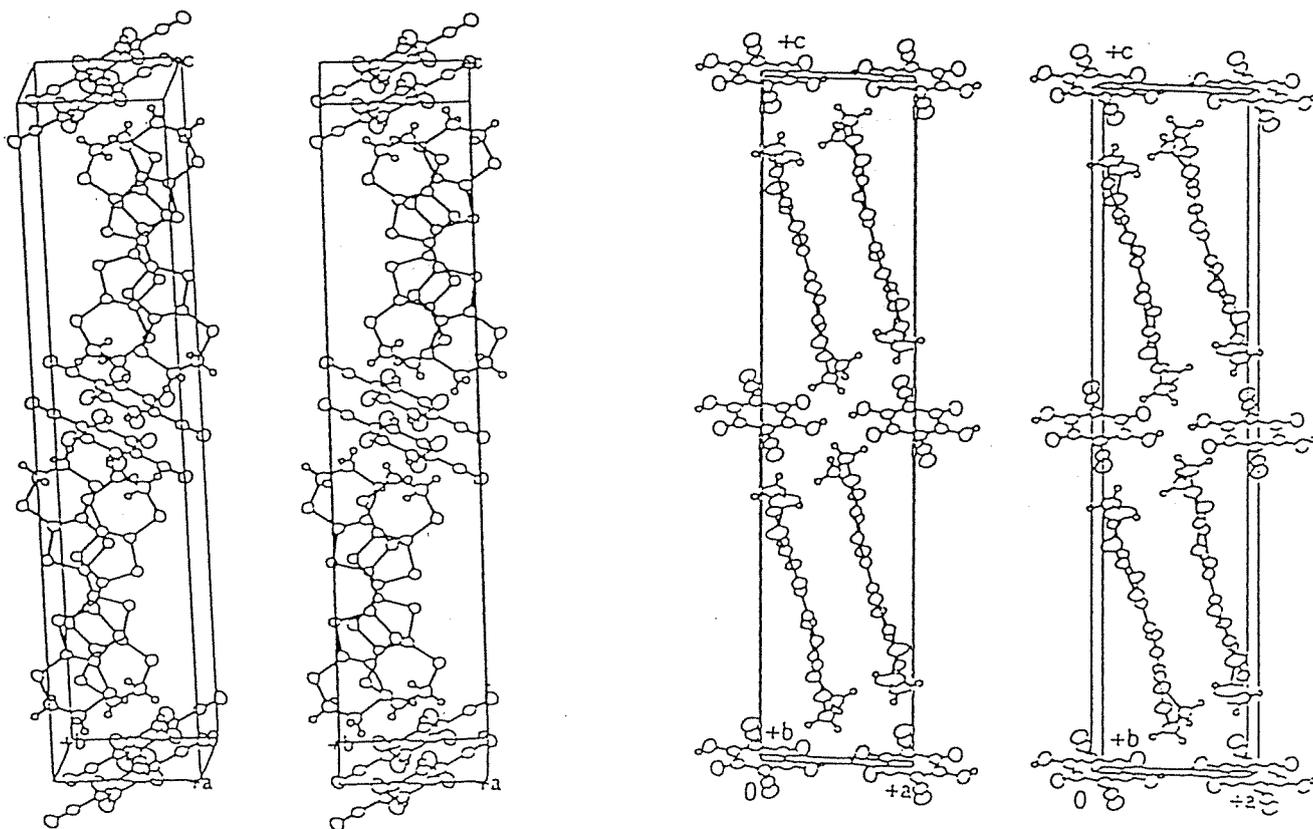
Furthermore, ET and OMTTF also gave single crystals of CT complexes with HCNAL, which are suitable for X-ray crystal structure analysis. The structures of these complexes were successfully solved.



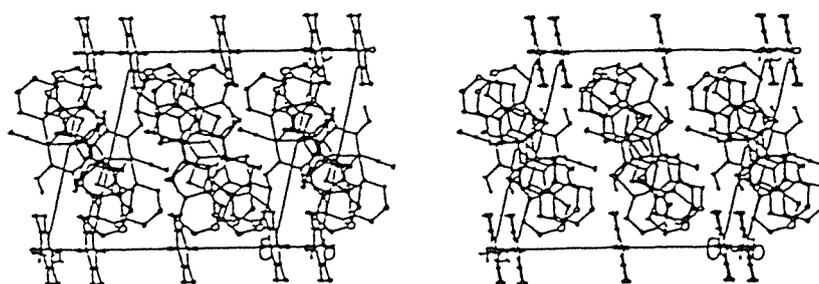
The stereoview of the crystal packing of the TMTTF, ET and OMTTF with HCNAL are shown below:



The crystal structure of (TMTTF)₂HCNAL



The crystal structure of $(\text{ET})_2\text{HCNAL}$



The crystal structure of $(\text{OMTTF})_3(\text{HCNAL})_2$

The infrared spectra of the TMTTF, ET and OMTTF with HCNAL complexes show the $\text{C}\equiv\text{N}$ stretching mode at around 2192 cm^{-1} , 2205 cm^{-1} and 2204 cm^{-1} , respectively. The degree of charge-transfer was calculated as 0.69, 0.48 and 0.49, respectively, by using the $\text{C}\equiv\text{N}$ stretching frequency of the $\text{Na}^+\text{HCNAL}^-$ and the neutral CNAA. The charge-transfer bands of these complexes are low energy band, i.e., less than 4500 cm^{-1} . This indicates the ionic nature of the complexes.

The room temperature conductivity of single crystal of $(\text{TMTTF})_2\text{HCNAL}$

and $(\text{ET})_2\text{HCNAL}$ complexes were found to be 0.03 Scm^{-1} and 0.83 Scm^{-1} , respectively. Investigation of the temperature dependence of the d.c. conductivity (between 305.5 and 140.0 K) points out an activation energy are 0.052 eV and 0.014 eV, respectively. The $(\text{OMTTF})_3(\text{HCNAL})_2$ complex shows the insulating behavior ($2.6 \times 10^{-6} \text{ Scm}^{-1}$).

The temperature dependence of the static magnetic susceptibility of several single crystals of $(\text{TMTTF})_2\text{HCNAL}$ has been studied over the range of 4.5-400K. The spin susceptibility $\chi(T)$ has broad maximum around $T_{\text{max}} \sim 270\text{K}$ and the value at room temperature is about $8 \times 10^{-4} \text{ emu mol}^{-1}$. The feature with a broad peak proves the presence of localized spin ($S=1/2$) coupled by antiferromagnetic interactions in the one dimensional frame, taking into account the semiconductive properties of this compound.

審査結果の要旨

バドルツザマン君の博士論文内容は、新しいアクセプターを設計・合成して、その種々の電荷移動錯体を合成し、各種スペクトルの測定や結晶構造解析によって物性を調べ、新しい分子性導体を開発する研究である。

2,3-ジクロロ-5,6-ジシアノベンゾキノン (DDQ) はベンゾキノン型の強い電子アクセプターであり、これまで分子性導体の構成分子として重要な役割を果たしてきた。このアクセプターを基本にして対称中心性を持つ異性体、2,5-ジクロロ-3,6-ジシアノベンゾキノン (CDDQ) を新しいアクセプターとして分子設計した。この分子は既知物質であったが、先ず、再現性のある合成法に改良した。ついで、このアクセプターとTTF型ドナー、芳香族アミンおよび芳香族炭化水素との電荷移動錯体を多数合成し、種々の物性を検討した。現在のところ、錯体の結晶構造解析は芳香族炭化水素との電荷移動錯体で得られているのみであるが、比較的伝導度の高い錯体が得られており、CDDQが今後この分野で重要なアクセプターとなり得る可能性を示唆する実験結果を得た。

次に、水素結合のドナー部分とアクセプター部分を合わせ持つベンゾキノン系アクセプターとしてシアニル酸を分子設計した。この分子についても、先ず、再現性のある合成法を確立した。ついで、各種のTTF型ドナーとの電荷移動錯体を合成した。この場合にはTMTTF、ET、およびOMTTFの三種類の錯体の結晶構造解析に成功した。特に注目されるのは、アクセプターのバックギングが三種類の錯体において異なっていることである。このことは、多種類の他のドナーとも変化に富んだ固有の構造を与える可能性のあることを示唆している。さらに、それぞれの錯体の各種スペクトル、および物性測定を行い、伝導性と結晶構造の関係についての知見を得ている。

以上の研究は、分子の設計から合成および結晶構造解析、各種スペクトルと物性の測定と非常に広範囲の化学にまたがるものであり、確実な合成法の開発と困難を克服して電荷移動錯体を合成し、その総合的な物性検討とその解釈を行っており、数物科学研究科構造分子科学専攻の博士論文としての内容に充分値すると判断した。新しい展開が容易に見えている重要なアクセプターを開発したことになり、今後この分野で大いに活用されるものと期待される。

また、バドルツザマン君に対し学位論文に係わる専門分野および基礎となる分野の学識を口述により試験した。分子性導体の発展の経過、新しい分子の設計の意義、合成の改良における問題点をどのように解決したか、電荷移動錯体の合成をどのように工夫したか、その錯体の各種スペクトルと結晶構造からどのように構成分子のイオン化度を見積もったか、今後の問題点と発展性などである。これらの質疑に関し、おおむね的確な答を得た。また論文中議論の不足している部分があること、解釈に疑問があることなどの指摘を受けた点は改訂された。

以上のように、博士論文内容を中心として、合成から物性の測定・解釈まで幅広く修得し、広い範囲の学識を有しており、数物科学研究科、構造分子科学専攻の学位に充分に値すると判断した。論文は英語で書かれておりその能力も充分であると判断した。また、公開発表会による最終審査にも合格した。