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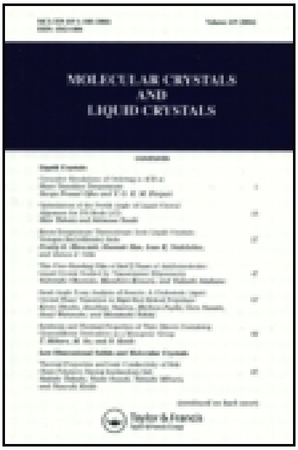

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Synthetic Conducting Materials: Charge Transfer Complex of 2,2′-butanediyl-bisisoquinolinium with TCNQ

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Synthetic Conducting Materials: Charge Transfer Complex of 2,2′-butanediyl-bisisoquinolinium with TCNQ

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2,2′-Butanediyl-bisisoquinolinium diiodide ($DIQC_4I_2$) *was synthesized by reaction of isoquinoline with 1,4-diiodobutane. This salt was further reacted with TCNQ and* $TCNQ^-$ *to obtain the charge transfer complex* $DIQC_4 \cdot TCNQ_3$*. This charge transfer complex was characterized by elemental analysis, infrared, electronic, and mass spectrometry. The crystal structure of* $DIQC_4 \cdot TCNQ_3$ *is triclinic with* $a = 8.1478(11)$, $b = 10.2302(13)$, $c = 15.041(2)\text{Å}$, $\alpha = 80.987(10)$, $\beta = 81.335(10)$, $\gamma = 70.402(10)$, $Z = 1$, *and space group* $P\bar{1}$*. The donors and acceptors are packed in segregated columns. The IR spectrum shows a very strong absorption envelope in the range of 4000 to 1000* cm^{-1} *resulting from the electronic conduction band. The electrical conductivity of* $DIQC_4 \cdot TCNQ_3$ *is* 2.4×10^{-2} S/cm *at room temperature with activation energy 0.20 eV, typical of semiconductor behavior.*

Keywords: charge transfer salt; organic conductor; TCNQ

INTRODUCTION

Intensive research activities on synthetic conducting materials have led to insights into their chemical and physical properties. The potential usefulness of conducting materials has been explored in many fields [1] such as molecular electronics, electronic switches, light emitting diodes, batteries, superconductors, and super-capacity. In the context of materials having high electrical conductivity, the need for

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planar molecules capable of close, highly ordered packing and stable radical ion configuration seems clear.

Aliphatic amines, aromatic amines, aromatic hydrocarbons and aromatic heterocycles are the major categories of organic donors [2]. Quinoline and isoquinoline are suitable for use as donors in charge transfer complexes with 7,7,8,8-tetracyanoquinone-dimethane (TCNQ). Many TCNQ charge transfer complexes are known to show metallic conducting behavior [3]. However, so far no work has been directed towards the synthesis of charge transfer complexes with N,N′-dialkyl-bisisoquinolines.

We have continued our interest in using heterocycles to synthesize charge transfer complexes with TCNQ. In this study we wish to report the synthesis and characterization of a charge transfer complex of 2,2′-butanediyl-bisisoquinolinium with TCNQ ($DIQC_4 \cdot TCNQ_3$). The crystal structure, spectroscopic, thermal, magnetic, and electrical properties of this complex are discussed.

EXPERIMENTAL

Synthesis

2,2′-Butanediyl-bisisoquinolinium diiodide ($DIQC_4I_2$) was prepared by reaction of isoquinoline with 1,4-diiodobutane in nitrobenzene. The $DIQC_4I_2$, TCNQ, and LiTCNQ was dissolved in mixture solvent of methanol and acetonitrile and heated on a thermostat water bath for 6 hours. The deep brown crystals were collected by filtration. [Elemental analysis: calculated for $C_{58}N_{14}H_{24}$ is $C\% = 75.24$, $H\% = 3.67$ and $N\% = 21.20$; found $C\% = 75.29$, $H\% = 3.86$ and $N\% = 21.18$.]

Physical Method

Infrared and electronic spectra were recorded on a Bio-Rad FTS-40 and Shimadzu UVPC-3101 spectrophotometer, respectively. Magnetic susceptibility measurements were carried out on a powdered sample by using a Quantum Design MPMS SQUID magnetometer. Electron paramagnetic resonance spectra were obtained on a Bruker ECS 106 EPR spectrophotometer. Thermal properties were measured using MAC Science DSC 3300 and Polymer Science TGA instruments. A Siemens P4 X-ray diffractometer was used to determine the crystal and molecular structure. Electrical properties were measured by employing a two-probe method with Keithley 617, 485, and 177 electrometers.

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RESULTS AND DISCUSSION

Crystal Structure

The crystal structure of $DIQC_4 \cdot TCNQ_3$ is triclinic with $a = 8.1478(11)$, $b = 10.2302(13)$, $c = 15.041(2)\text{Å}$, $\alpha = 80.987(10)$, $\beta = 81.335(10)$,

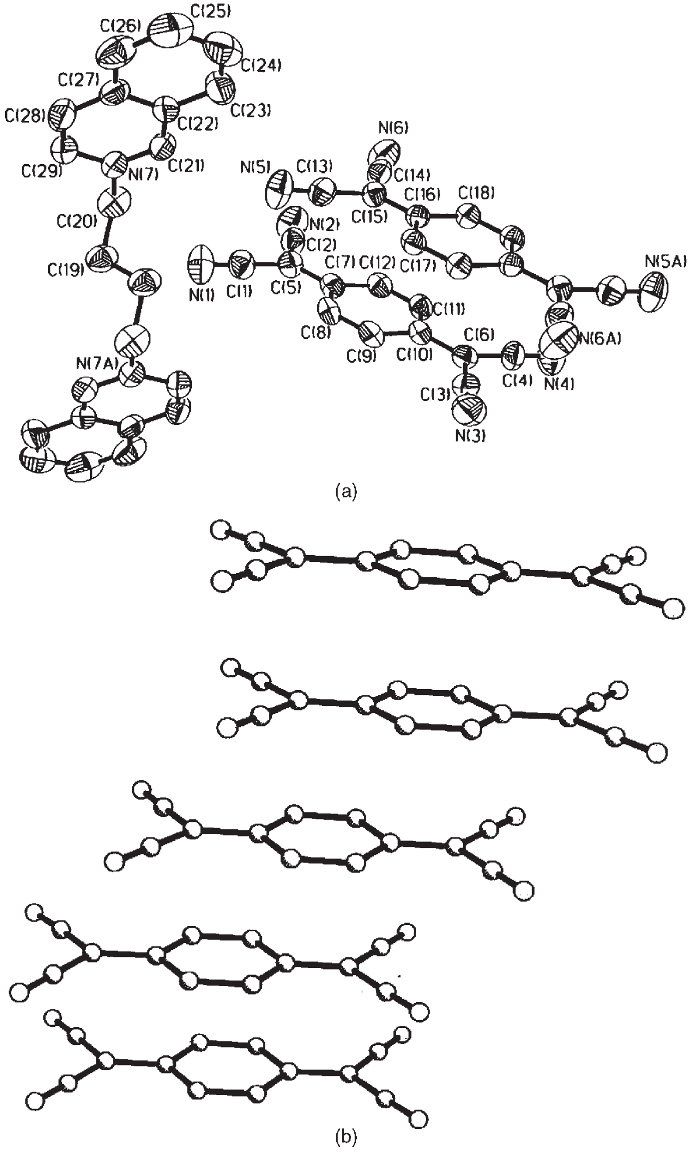
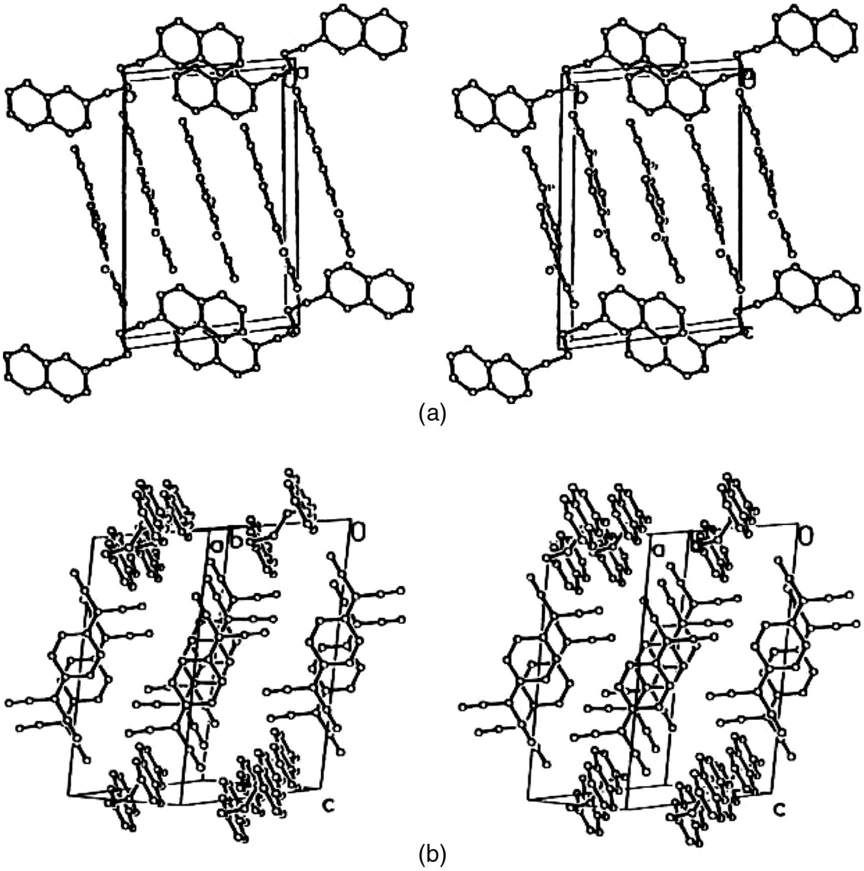


FIGURE 1 ORTEP diagram of the X-ray crystal structure of $[DIQC_4 \cdot TCNQ_3]$ and the stacking packing of TCNQ in the TCNQ column.

$\gamma = 70.402(10)$, $Z = 1$, and space group $P\bar{1}$. The crystal structure of $\mathrm{DIQC_4 \cdot TCNQ_3}$, cationic $\mathrm{DIQC_4^{2+}}$ and anionic $\mathrm{[TCNQ]_3^{2-}}$ is shown in Figure 1. Each molecular cation has a C_4 alkyl chain, which is perpendicular to the isoquinoline ring. $\mathrm{[DIQC_4 \cdot TCNQ_3]}$, has segregated packing in which the TCNQ column is intercalated into the spacing of two $\mathrm{DIQC^{2+}{}_4}$ layers. Two stacking types of TCNQ are found in the TCNQ column. The inter-planar distance of two TCNQ molecules is 3.220 Å in the ring-ring stacking and 3.422 Å in the ring-bond stacking, respectively. The molecular packing in the unit lattice is shown in Figure 2.



(a)

(b)

FIGURE 2 Molecular packing of $\mathrm{[DIQC_4 \cdot TCNQ_3]}$ in a unit cell.

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Electrical Conductivity

A two-probe variable temperature electrical conductivity measurement for a pressed powder pellet of [$DIQC_4 \cdot TCNQ_3$] is shown in Figure 3. The electrical conductivity of [$DIQC_4 \cdot TCNQ_3$] at room temperature is 2.4×10^{-2} S/cm. The electrical conductivity of this charge transfer complex follows the equation

$$\sigma = \sigma_o e^{-E_a}/kT$$

in which E_a is activation energy. The [$DIQC_4 \cdot TCNQ_3$] complex presents thermally activated conductivity that is a characteristic behavior of semiconductors. The activation energy obtained by least square fitting is 0.20 eV.

Electronic Absorption

The solution state ultraviolet-visible absorption spectrum of [$DIQC_4 \cdot TCNQ_3$] complex is shown in Figure 4. A freshly prepared acetonitrile solution was used in this measurement. TCNQ has an absorption band at 394 nm and $TCNQ^-$ has absorption bands at 840 nm and 394 nm. The ratio of $A_{(394)}/A_{(840)}$ can be used to determine

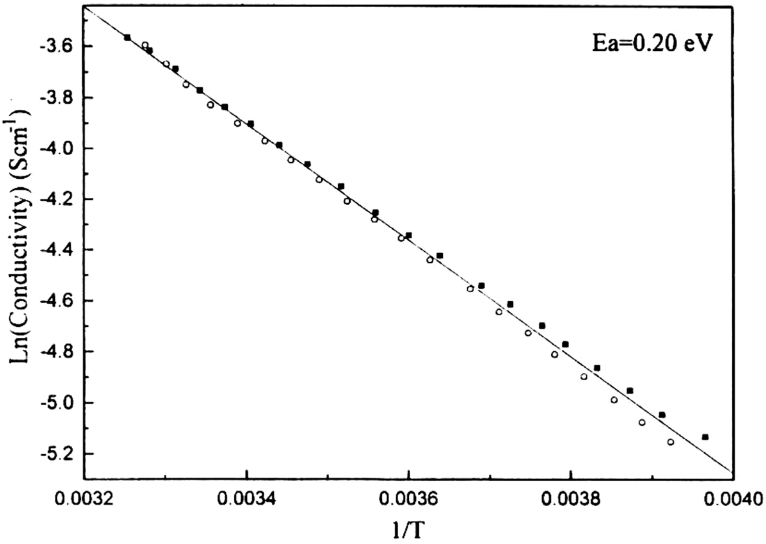

FIGURE 3 Electrical conductivity plotted against reciprocal temperature for [$DIQC_4 \cdot TCNQ_3$]. (○ – measurement in increasing temperature; ■ – measurement in decreasing temperature.)

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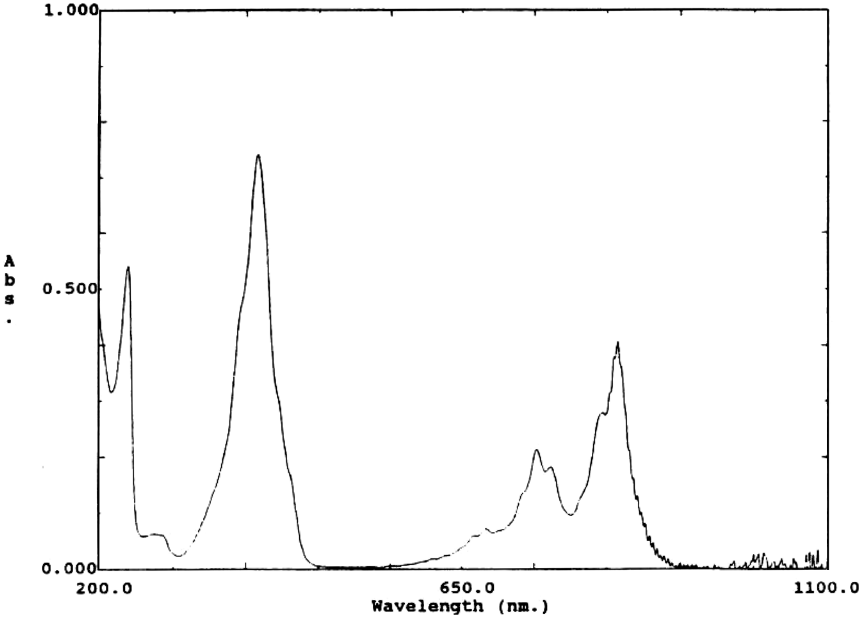

FIGURE 4 Electronic absorption spectrum of [DIQC_4 · TCNQ_3] in methanol solution.

the molar ratio of TCNQ to $TCNQ^-$ in charge transfer complexes [4]. In [DIQC_4 · TCNQ_3] complex a $A_{(394)}/A_{(840)}$ ratio of 1.03 was observed, clearly indicating that the molar ratio of TCNQ to $TCNQ^-$ is 1:2 in this substance. This result is consistent with the X-ray crystal structure analysis.

Magnetic Properties

Temperature dependence of the magnetic susceptibility and magnetic moment of [DIQC_4 · TCNQ_3] are shown in Figure 5. At high temperature (up to 100 K) the susceptibility follows the Curie law; but below this temperature it begins to deviate from the Curie law. At low temperature the susceptibility of this complex salt shows a strong antiferromagnetic coupling typical of highly conducting TCNQ salts [5].

Thermal Analysis

The differential scanning calorimetric graph of [DIQC_4 · TCNQ_3] is shown in Figure 6. The first and second cyclic running between 40°C

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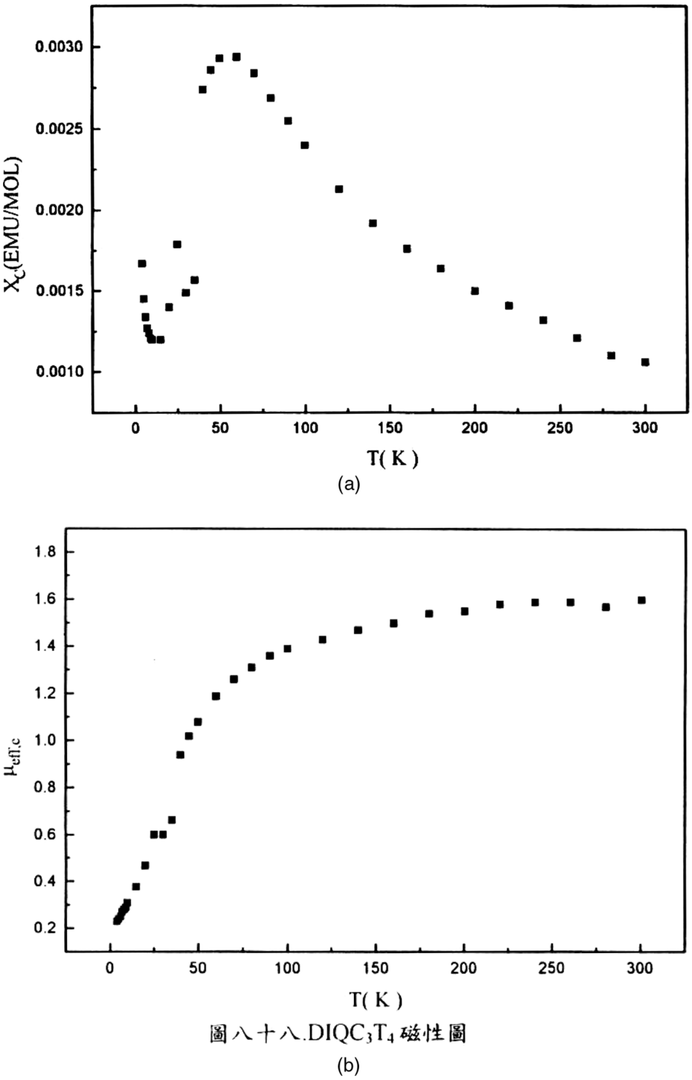

FIGURE 5 Temperature dependence of magnetic susceptibility and magnetic moment of [$DIQC_4 \cdot TCNQ_3$] in temperature range of 5 K to 300 K.

and 250°C shows no phase transition. The third run from 40°C to 350°C shows an endothermic peak at 265°C and following this a successive exothermic peak at 276°C. The thermal gravimetric analysis shows that no weight was lost before 270°C and a gradual weight loss

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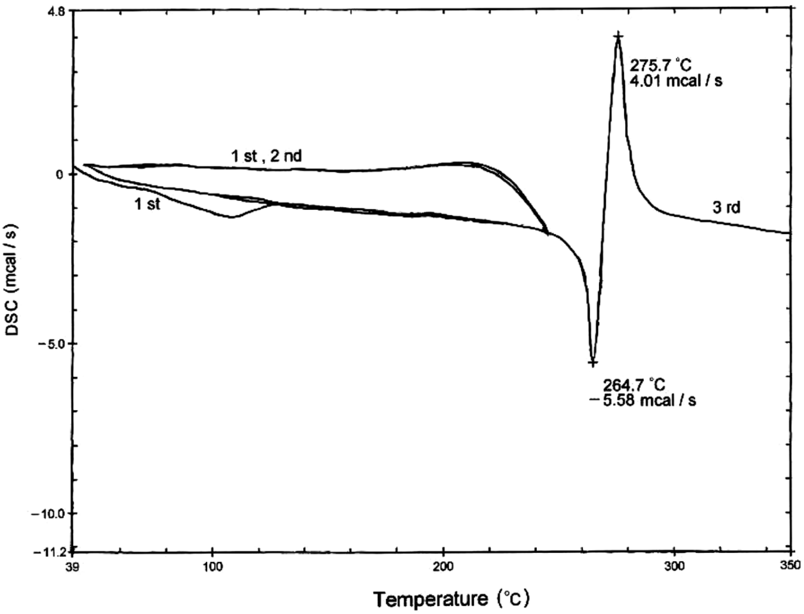

FIGURE 6 Differential scanning calorimetric graph of [$DIQC_4 \cdot TCNQ_3$].

was observed after 270°C. These results indicate that the [$DIQC_4 \cdot TCNQ_3$] complex melts to liquid at 265°C. The liquid phase exists for a short period and then decomposes after 276°C. Flash heat treatment of [$DIQC_4 \cdot TCNQ_3$] shows that this complex could be recrystalized from the liquid phase without changing its electrical conductivity. Results of thermal analysis show that [$DIQC_4 \cdot TCNQ_3$] is suitable for use as a solid electrolyte in supercapacitors containing organic semiconducting electrolyte.

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