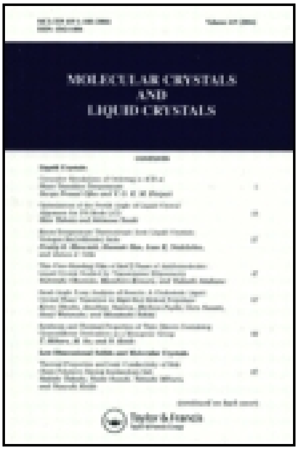

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of Charge-Transfer Complexes of Π-Acceptor TCNQ with Various Phenols

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To cite this article: Neelu Chouhan, M. L. Kalra, Sudhish Kumar, Y. N. Singh & Suresh C. Ameta (2007): Synthesis and Characterization of Charge-Transfer Complexes of Π-Acceptor TCNQ with Various Phenols, Molecular Crystals and Liquid Crystals, 469:1, 99-110

To link to this article: http://dx.doi.org/10.1080/15421400701431778

Mol. Cryst. Liq. Cryst., Vol. 469, pp. 99–110, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701431778

Synthesis and Characterization of Charge-Transfer Complexes of Π-Acceptor TCNQ with Various Phenols

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The charge-transfer complexes of formula $D(TCNQ)_2$ *are formed between π-acceptor TCNQ (7,7′,8,8′-tetracyanoquinodimethane) and phenolic donors such as p-aminophenol, α-naphthol, 2,4,5-trichlorophenol, and p-cresol. Solution growth and an electrochemical method were used to synthesize the complexes. Their structural analyses were performed using elemental analysis (C, H, N, and halogen), X-ray diffraction (XRD) patterns, scanning electron microscope (SEM) photographs, dc electrical conductivity, and spectral properties (electronic and* ^1H *NMR), which reveals that these quasi-one-dimensional monoclinic crystalline compounds are synthesized in the single phase with space group* $P_2/_{1/n}$ *and are of semiconductor nature at room temperature. The stoichiometric ratio of donor and acceptor in the complex* $D(TCNQ)_2$ *is found to be in a 1:2 ratio, respectively.*

Keywords: charge-transfer complex; dc electrical conductivity; electrochemical method; quasi-one-dimensional conductor; SEM; solution growth method; TCNQ; XRD

INTRODUCTION

The π-electron acceptor TCNQ (7,7′,8,8′-tetracyanoquinodimethane) [1] forms conducting materials with various aromatic donors that

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possess very interesting physical properties such as high anisotropy, low density, and low dimensional-metal-like electrical transport properties. Recently studied TCNQ salts such as BADM–TCNQ complex (BADM = bianthracene-9,10-dimethylene) [2] show thermochromism and photochromism. Charge-transfer complexes of TCNQ with some drugs [3,4] such as ofloxacin, levofloxacin, lomefloxacin, pipemidic acid, ciprofloxacin, norfloxacin, perfloxacin, and fleroxacin show antibacterial and biological activities more than the parent drug itself, making them pharmaceutically more important. Magnetic properties of porphyrinogen TCNQ electron-transfer salts of copper(II) and nickel(II) [5], elastomeric charge-transfer complexes of ionene–TCNQ [6], and molecular conductor (2-[2-1H-benzimidaxolyl]-1H benzimidazolium) TCNQ [7] grown by electrocrystallization show metal–semiconductor and semiconductor–insulator transitions. Switching and memory phenomena were observed in $Cu(TCNQ)_2$ [8], $Qn(TCNQ)_2$ [8], and $Cs_2(TCNQ)_3$ [9], showing metallic conductivity at room temperature, and $Mn((MAC)(TCNQ)_2)$ [10] (MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18,2.12)14,16-pentaene) exhibits antiferromagetism with conductive nature. ET-$(TCNQ)_2$ (ET = bis(ethylenedithio tetrafulvalene)) [11] is a two-dimensional polymorphic conductor that shows metal-like conducting properties. In the present work, charge-transfer complexes of acceptor TCNQ were synthesized with phenolic donors (p-aminophenol, α-naphthol, 2,4,5-trichlorophenol, and p-cresol) using the solution growth and electrochemical methods. The complexes exhibit very interesting crystallographic properties and dc electrical conductivity and are characterized by elemental analysis, UV-vis, and ^1H NMR spectral studies as well as X-ray diffraction and SEM studies.

EXPERIMENTAL

All the chemicals used are of analytical-reagent grade. TCNQ (E Merck), α-naphthol (E Merck), 2,4,5-trichlorophenol (Fluka), p-cresol (E Merck), p-aminophenol (E Merck), and 18-6-crown ether (E Merck) were used for synthesis, and their solution is prepared in dry acetonitrile solvent. The solvent acetonitrile was dried for 1 day over dry silica, refluxed for 5 h over P_2O_5, distilled through a fractionating column middle fraction (bp 82°C), and collected in air-free bottles.

Melting points of grown complexes was determined in open capillaries and are uncorrected. Elements C, H, N, and Cl were estimated using a Heraeus-Vario-EL III-Carlo-Erba 1108 analyzer. Electronic spectra of $D(TCNQ)_2$ were recorded with Systronics double-beam computerized spectrophotometer (model 2101). ^1H NMR spectra of complexes were taken on a DRX 300 (Bruker) spectrophotometer, using TMS as internal standard and wet acetone as solvent. The purity of compounds was checked on silica-gel G coated plates using iodine vapors as visualizing agents. XRD patterns were recorded at 15°C by a computerized XRD powder diffractometer, Rikagu Miniflex tabletop model (960129A26) with CuK_α radiations, to identify the crystalline phase. The cell parameters of crystals have been determined by indexing different peaks using known parameters of recorded XRD patterns with the help of the powder diffraction package Diffraction plus. SEM photographs of samples were taken by Liza electron optics model LEO-430.

The dc electrical conductivity of the complex (in the compressed pellet form) was measured, using a manually constructed furnance, Keithly's autoranging picoammeter, Systronics twin power supply, Keithly's 155 null detector microvoltmeter, Toshniwal's self-adjustable autotransformer (Variac), TWG Kontact thermometer, and Epoch's μ-Amicomp UPS.

RESULTS AND DISCUSSION

The elemental analyses and spectral data suggested that all complexes correspond to 1:2 stoichiometric ratios of donor and acceptor.

By keeping molecular size low, high polarizability, minimum columbic repulsion, fractional charge transfer (degree of charge transfer z, found at $0.5 < z < 1$), and uniform segregated stacking were obtained in the charge-transfer complexes. Low-molecular-weighted phenols with variety of functional groups of different Hammett to parent skeletons of phenol were used as donors for the present study.

For good crystal growth, a slow rate of growth; minimal disturbances such as temperature variation, mechanical variation, and intermittent intense light exposure; slow nucleation, an extremely clean and dry container with highly purified (crystallized 7 to 9 times), and dried solid precursors were used for the synthesis. In the solution growth method of synthesis [12], the acceptor and donor solution (in dry acetonitrile solvent) was mixed in a 1:2, donor–acceptor ratio in a hot condition, then cooled slowly to allow the chemical reaction to take place and crystallize. Then the container was left undisturbed at constant temperature and in an inert environment for the duration, which may be up to a week or month, according to the needs of the crystallization process. During the electrochemical synthesis method [13], acceptors and donors were separately dissolved in 50 ml of dry acetonitrile solvent, in a stoichiometric ratio, and then poured into the cathode and anode compartments of the H-cell respectively. Then

10 mL of 0.1 M 18-6-crown ether (supporting electrolyte) was added in each arm of the cell, and 20 miliamperes of current were passed for 5 to 7 days. Colorful crystals were deposited on cathode, washed with dry benzene and carbontetrachloride, and recrystallized by acetonitrile. The crystals obtained were almost insoluble in most of the solvents.

The dc electrical conductivities and other physical analyses of TCNQ and its salts are shown in Table 1. The general behavior of dc electrical conductivity obeys the relation $\sigma = \sigma_o \exp(-E_a/KT)$, where σ_o is constant, E_a is the activation energy of the conduction process, T is the absolute temperature, and K is the Boltzmann constant. The room-temperature dc electrical conductivity of the complexes lies in the range 7.87×10^{-12} to 1.79×10^{-6} S cm^{-1}. The activation energy of electrical conduction is found in the range 0.0921 to 0.4199 eV, depending on varying temperature. An exponential relationship between $\log \rho$ and 1000/T has been observed, which indicates the semiconductor behavior of the complexes with some transitions. In the low-temperature region, the slopes of plots here were very small value because of extrinsic conduction present in them, but at higher temperature, a high value of the slope was observed because the complex behaves as an intrinsic semiconductor. Dc electrical conductance dependence of D(TCNQ)$_2$ salts on the temperature was interpreted on the basis of electron–phonon interactions [14], disorder, the impurity effect at low temperature, and the scattering effect due to impurities. This electronic correlation also plays an important role in deciding the sharpness of transitions.

Electronic Spectra of D(TCNQ)$_2$

Electronic (UV-vis) spectra of D(TCNQ)$_2$ complexes possess α-, β-, and charge-transfer bands, and their values are tabulated in Table 2. On comparison with standard data [15–17] reported with TCNQ complexes, it is confirmed that the complex belongs to the D(TCNQ)$_2$ category.

^{1}H NMR Study

The ^{1}H NMR spectrum of pure TCNQ exhibits a hump with two additional signals at δ 7.150 and 8.028. The complex of p-aminophenol shows additional signals at δ 7.88 and 8.15, which were associated with aromatic hydrogen. The complex of α-naphthol gives the peak of −OH proton at δ 9.15 and double doublet of four H of TCNQ at δ 7.30, 7.27, 7.36, and 7.39. Some peaks of C_{8H} at δ 8.15, C_{5H}

TABLE 1 Analytical and Physical Data of the D(TCNQ)$_2$ Complexes

D(TCNQ)$_2$ complex of donor (method)	C% found (calculated)	H% found (calculated)	N% found (calculated)	σ_{RT} (Scm^{-1})	E$_a$ (eV)	Molecular formula	Color
TCNQ (Pure)	64.28	2.38	33.34	2×10^{-12} (25°C)	0.6000	$C_9H_4N_4$	Rusty brown
p-Aminophenol (solution growth)	68.09 (69.63)	3.02 (2.90)	23.32 (24.37)	4.36×10^{-7} (20°C)	0.1650	$C_{30}H_{15}N_9O$	Greenish black
p-Aminophenol (electrochemical)	69.50 (69.63)	2.89 (2.90)	24.41 (24.37)	1.79×10^{-6} (20°C)	0.1288	$C_{30}H_{15}N_9O$	Brownish black
α-Naphthol (solution growth)	73.34 (73.60)	2.99 (3.22)	21.06 (20.22)	7.87×10^{-12} (27°C)	0.1105	$C_{34}H_{18}N_8O$	Shiny black
α-Naphthol (electrochemical)	73.60 (73.60)	3.05 (3.22)	20.62 (20.22)	8.99×10^{-8} (27°C)	0.0872	$C_{14}H_{18}N_8O$	Shiny black
2,4,5-Trichlorophenol (solution growth)	59.40 (59.45)	1.81 (1.82)	9.89 (18.50)	5.13×10^{-10} (30°C)	0.4199	$C_{30}H_{11}N_8Cl_3O$	Dark red
p-Cresol (solution growth)	72.28 (72.09)	3.16 (3.10)	20.72 (21.7)	1.41×10^{-11} (30°C)	0.0920	$C_{31}H_{16}N_8O$	Reddish black

TABLE 2 Electronic Spectra of $D(TCNQ)_2$ Complex

Donor (method of synthesis)	α-bands (nm)	β-bands (nm)	Charge-transfer bands (nm)
p-Aminophenol (solution growth)	391.60	663.60, 678.30, 741.43, 761.98	820.40, 842.30
p-Aminophenol (electrochemical)	393.20	663.77, 668.10, 741.34, 759.99	822.50, 844.39
α-Naphthol (solution growth)	393.20	663.77, 678.19, 741.54, 759.99	822.00, 845.00
α-Naphthol (electrochemical)	394.00	662.44, 677.91, 742.84, 760.23	822.0, 845.0
2,4,5-Trichlorophenol (solution growth)	393.48	662.38, 679.51, 741.54, 759.99	823.00, 844.00
p-Cresol (solution growth)	393.20	663.70, 679.50, 742.86, 759.99	824.80, 845.20
TCNQ (pure) [18]	393.21	642.55, 651.74, 744.88, 763.79	822.00, 845.00

at δ 7.80, C_{2H} at δ 6.75, and C_{3H}, C_{4H}, C_{6H}, and C_{7H} at δ 7.49, 7.50, 7.57, and 7.63, respectively, are found in the form of multiples. NMR signals of 2,4,5-trichlorophenol–TCNQ, found in the downfield region at δ 9.63 due to OH proton, and signals at δ 6.77, 6.97, 7.20, 7.25, 7.43, 7.46, 7.57, and 7.62 (multiplet) are due to aromatic H-signals. Finally, the p-cresol complex shows one signal of –OH hydrogen at δ 8.37 and one double doublet of four hydrogen of TCNQ at δ 6.70, 6.73, 6.97, and 6.99. A multiplet 21 signals due to aromatic H is in the range δ 7.10–8.00, and one singlet of $-CH_3$ hydrogen of p-cresol has been observed at δ 2.19.

XRD Study of Complex $D(TCNQ)_2$

The cell parameters of the sample have been determined by indexing different peaks in XRD patterns with the help of the standard XRD pattern [19]. The space group was detected from the systematic absence of h, k, and l indices. The density of the crystal is measured by the floatation method. Different peaks are indexed, using Bragg's law:

$$Q_{hkl} = \frac{1}{d^2} = (4\sin^2)\frac{\theta}{\lambda^2}$$

All the studied samples were synthesized in the single phase and belong to the monoclinic-type crystal system of space group $P_2/_{1/n}$ with value of parameter $z = 8$ (8 formula unit per unit cell) and $\mu = (CuK_\alpha, \lambda = 1.5406\,\text{Å}) = 7.20\,\text{cm}^{-1}$. The rest of the parameters are addressed in Table 3.

SEM Study

SEM pictures of $D(TCNQ)_2$ samples are shown in Fig. 1 (p-aminophenol pure), Fig. 2 (p-aminophenol-$(TCNQ)_2$), Fig. 3 (7,7′,8,8′-tetracyanoquinodimethane pure), Fig. 4 (α-naphthol-$(TCNQ)_2$), Fig. 5 (α-naphthol

TABLE 3 Cell Parameters of $D(TCNQ)_2$ Complex

Donors	a (Å)	b (Å)	c (Å)	β (°)
p-Aminophenol	7.85	17.50	17.87	91.52
α-Naphthol	7.57	17.39	17.85	97.605
2,4,5-Trichlorophenol	7.08	17.55	17.92	94.967
p-Cresol	6.89	17.38	17.89	93.74
TCNQ (pure)	8.906	7.060	16.39	98.54

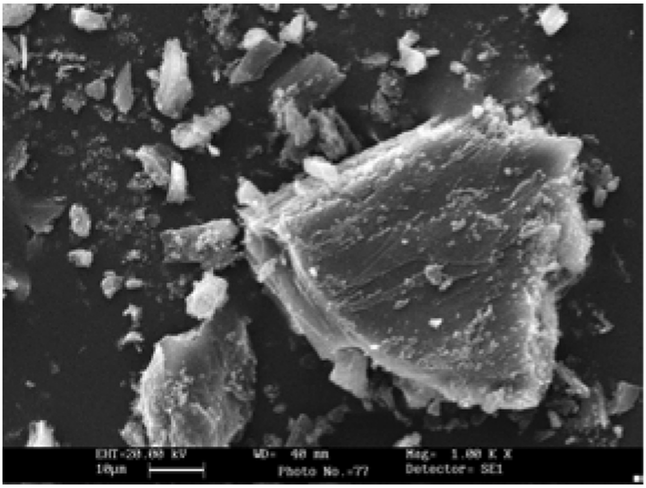

FIGURE 1 p-Aminophenol-TCNQ.

pure), Fig. 6 (2,4,5-trichlorophenol–$(TCNQ)_2$), and Fig. 7 (p-cresol-$(TCNQ)_2$). SEM photographs of precursors p-cresol and 2,4,5-trichlorophenol were not possible to picture, because of their low melting point. All samples are pictured with the same magnification (1000 times) on the 10 µm scale with 300-kV EHT, 40-mm WD, and detector SE_1. It is

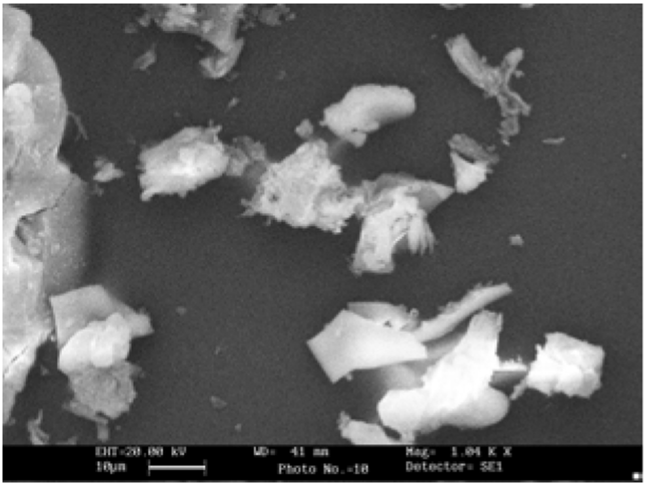

FIGURE 2 p-Aminophenol pure.

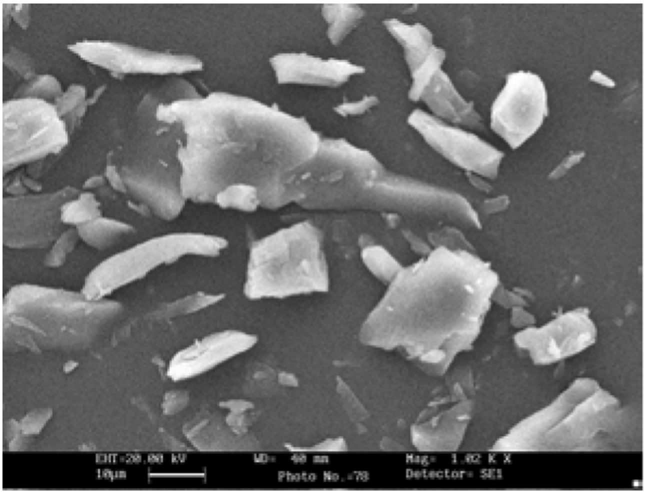

FIGURE 3 7,7′8,8′-Tetracyanoquinodimethane pure.

revealed from photographs that surface structure with particle size and shape of the synthesized complexes are totally different from their parent molecule. A more shiny appearance of the synthesized charge-transfer complexes is due to their more conductive behavior than their parent compounds.

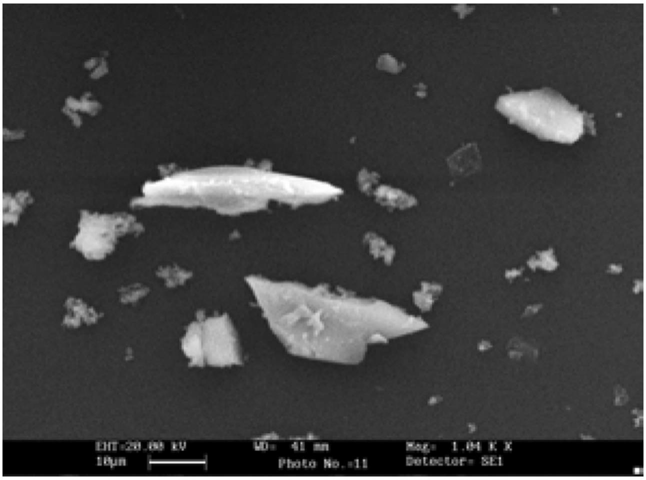

FIGURE 4 α-Naphthol-TCNQ.

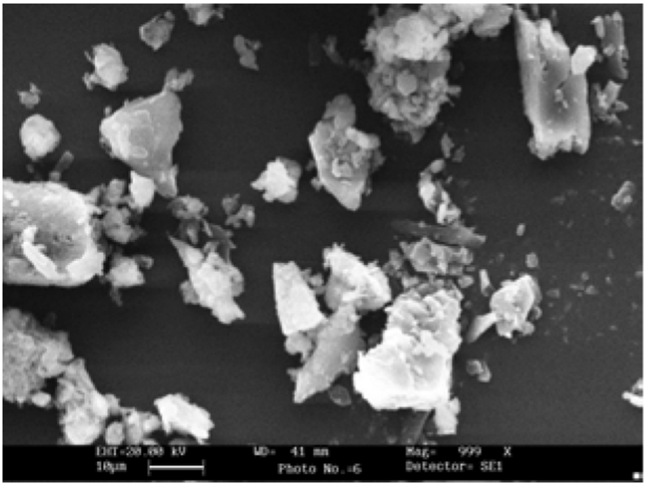

FIGURE 5 α-Naphthol pure.

CONCLUSION

Some of the major conclusions that summarize the achievements of the present study and scope for the future are as follows:

Chemical analyses and optical observations of the complexes confirms the stoichiometric donor–acceptor ratio 1:2 and the presence of

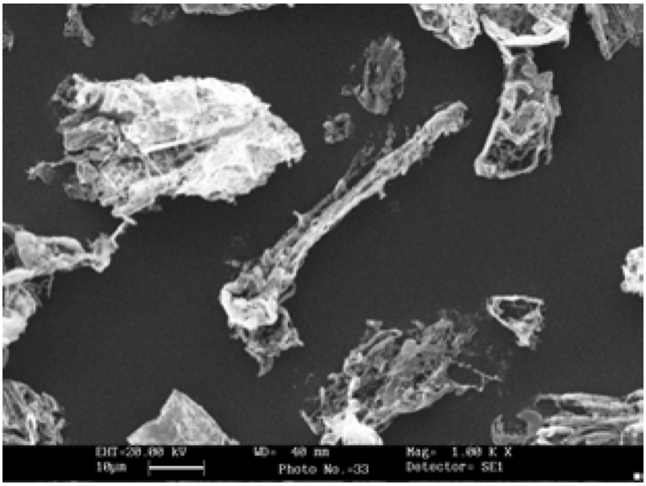

FIGURE 6 2,4,5-Trichlorophenol-TCNQ.

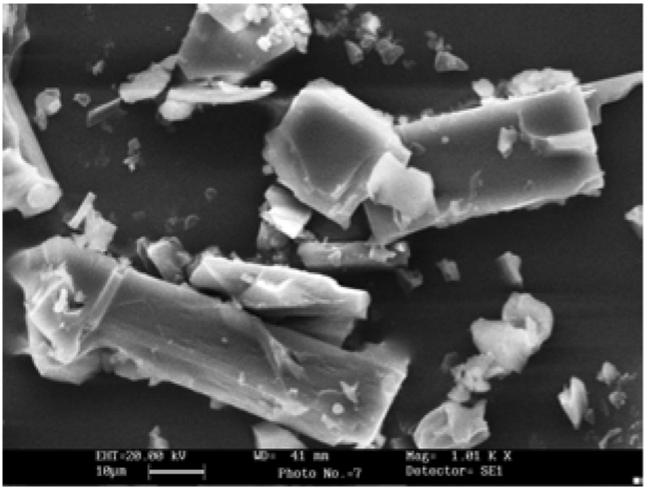

FIGURE 7 p- Cresol-TCNQ.

TCNQ° and $TCNQ^-$ moieties in $D(TCNQ)_2$ complexes. XPD study of $D(TCNQ)_2$ complexes shows that these crystalline complexes are formed in a single phase with space group $P_{2/1/n}$, and all complexes belong to the monoclinic type of crystal systems. On comparing analytical and spectral data obtained for the $D(TCNQ)_2$ complexes grown by different methods (solution growth and electrochemical), it is found that complexes are structurally the same but physically different (color, crystal size, electrical conductivity) except that, all studied complexes shows semiconductor behavior at room temperature with comparative lower activation energy than metallic compounds. Kamras et al. [20] explained the effect of the method of synthesizing salts on conductivity that we observed here. The general observation about the $D(TCNQ)_2$ complexes are that complexes grown by the electrochemical method are more conductive, which means that these complexes were more pure than the same grown by solution growth, which was also verified by the temperature-dependent behavior of the complex on electrical conductivity. It is also speculated that impurities and disorder act as the excess potential [21], and the overall effect is reduction of conductivity, as found in complexes grown by the solution growth method. This reduction depends on the strength and distribution of the impurity potential. One major observation about the electrical transport property dependence on temperature is that all $D(TCNQ)_2$ complexes belong to the class of quasi-one-dimensional organic systems.

ACKNOWLEDGMENTS

This work was supported by a research grant from University Grants Commission (UGC), Bhopal, to one of the authors (N. C.). Authors are thankful to Regional Sophisticated Instrumentation Center (RSIC), Central Drug Research Institute (CDRI), Lucknow, for instrumental facilities and to N. Laxmi, S. R. Jakhar, and I. J. Singhvi of ML Sukhadia University, Udaipur, India, for providing necessary help in investigations.

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