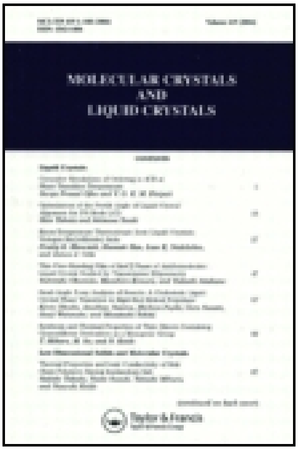


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Charge Transfer Complexes of 3, 3′, 5, 5′-Tetra-Phenyl-2, 2′-Dithiodipyranylidine (2, 2′ DIPSØ$_4$) with 7, 7′, 8, 8′-Tetracyanoquinodimethane (TCNQ) And Iodine

Zhu Daoben (Chu Tao-Pen) [a] , Wan Meixiang [a] , Li Mingzhu [a] , Guo Dian [a] & Qian Renyuan [a]
[a] Institute of Chemistry Academia sinica, China

To cite this article: Zhu Daoben (Chu Tao-Pen) , Wan Meixiang , Li Mingzhu , Guo Dian & Qian Renyuan (1982): Charge Transfer Complexes of 3, 3′, 5, 5′-Tetra-Phenyl-2, 2′-Dithiodipyranylidine (2, 2′ DIPSØ$_4$) with 7, 7′, 8, 8′-Tetracyanoquinodimethane (TCNQ) And Iodine, Molecular Crystals and Liquid Crystals, 86:1, 57-62

To link to this article: http://dx.doi.org/10.1080/00268948208073668

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, pp. 57–62
0026-8941/82/8601-0057$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

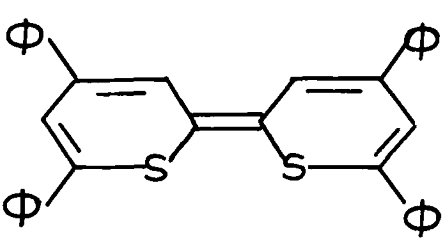
CHARGE TRANSFER COMPLEXES OF3,3',5,5'-TETRAPHENYL-2,2'-DITHIODIPYRANYLIDINE(2,2'DIPS$\emptyset_4$) WITH 7,7',8,8'-TETRACYANOQUINODIMETHANE(TCNQ) AND IODINE

ZHU DAOBEN (CHU TAO-PEN), WAN MEIXIANG, LI MINGZHU, GUO DIAN and QIAN RENYUAN
Institute of Chemistry
Academia sinica, China

Received for publication August 17, 1981

New charge transfer complexes of 2,2'DIPS$\emptyset_4$ with TCNQ and iodine have high conductivity at room temperature. VSC mesurements showed a broad maximum centered at 223K and a large narrow maximum centered at 273K for 1:1, 1:2 TCNQ complexes respectively.

Since the discovery of charge transfer complex of tetrathiafulvalene(TTF)-7,7',8,8'-tetracyanoquinodimethane(TCNQ) to display unusual metal-like properties, there has been numerous attempts to find new organic metals. We have recently prepared new organic charge transfer complexes of 2,2'DIPS$\emptyset_4$ with TCNQ and iodine and studied their physical properties.



2,2'DIPSΦ_4

SYNTHESIS AND CHARACTERIZATION

The solution of acetophenone and morpholine in toluene was refluxed to give colorless liquid morpholine-1-phenylethylene, then reacted with carbon disulphide to yield thiopyranthione,MS: m/e 280(78, M$^+$), 236(100); IR (KBr): 1590,1570,1475,1440,1380, 1320,1230,1210,1050,990,760,695 cm^{-1}. 2,2'DIPSØ$_4$ was obtained by heating 3,5-diphenyl-thiopyran-2-thione with copper powder in xylol, MS: m/e 496(96, M$^+$), 375(14), 248(14); IR (KBr): 1595,1490, 1445, 1365, 1260, 1180, 1070, 1030, 840,750,690 cm^{-1}; UV(CH$_3$CN): 268nm(4.652), 304nm(4.540), 360nm (3.880), 528nm(3.590). It absorbs more strongly than TTF at all wavelength between 250-700nm, suggesting that this donor is more polarizable than TTF. Electrochemical analysis showed that it has very low halfwave potentials $E'_{1/2}$=0.23v, $E''_{1/2}$= 0.39v, ΔE=0.16v. The data are compared with those of TTF,TTFØ$_4$, 4,4'DIPSØ$_4$ and 4,4'DIPØ$_4$ in TABLE 1.

Single crystals of 2,2'DIPSØ$_4$I$_{2.41}$ were obtained both by electrocrystallization procedure (2,2'DIPSØ$_4$ in CH_2Cl_2 solution containing Bu_4NI, constant current with Pt electrodes) and slow cooling method (2,2'DIPSØ$_4$ in hot CH_2Cl_2 mixed with I_2 in hot CH_2Cl_2). UV(CH_3CN): 248(4.443),356(3.723), 532nm(3.505); IR (KBr): 1650,1570,1470,1440,1340, 1135,959,830,750,680 cm^{-1}. X-ray analysis showed that it is tetragonal with unit cell parameters

TABLE 1. Comparison of halfwave potentials

	$E'_{1/2}$	$E''_{1/2}$	$\Delta E_{1/2}$	Ref.
4,4'DIPSØ$_4$	+0.22	+0.41	0.19	[1]
2,2'DIPSØ$_4$	+0.23	+0.39	0.16	this work
4,4'DIPØ$_4$	+0.15	+0.47	0.32	[1]
TTF	+0.32	+0.70	0.38	[2]
TTFØ$_4$	+0.40	+0.73	0.33	[2]

a=b=19.64(7)Å, c=3.80(4)Å. The resonant Raman spectrum of DIPSØ$_4$I$_{2.41}$ complex shows a strong band at 113cm^{-1} characteristic of the symmetric mode of I_3^-. 2,2'DIPSØ$_4$ was reacted with TCNQ in 1:1, 1:2 mol. ratios respectively in acetonitrile to give 1:1 and 1:2 complexes. UV(CH$_3$CN) for 1:1 complex 392nm(4.513), 840nm(4.356); for 1:2 complex 392nm(5.036), 840nm(4.310); IR (KBr) for 1:1 complex 2180,1570,1470,1350,1150,1000,830,750,690 cm^{-1}; for 1:2 complex 2180,1990,1560,1460,1320, 1150,830,750,680,500 cm^{-1}.

ELECTRICAL CONDUCTIVITIES

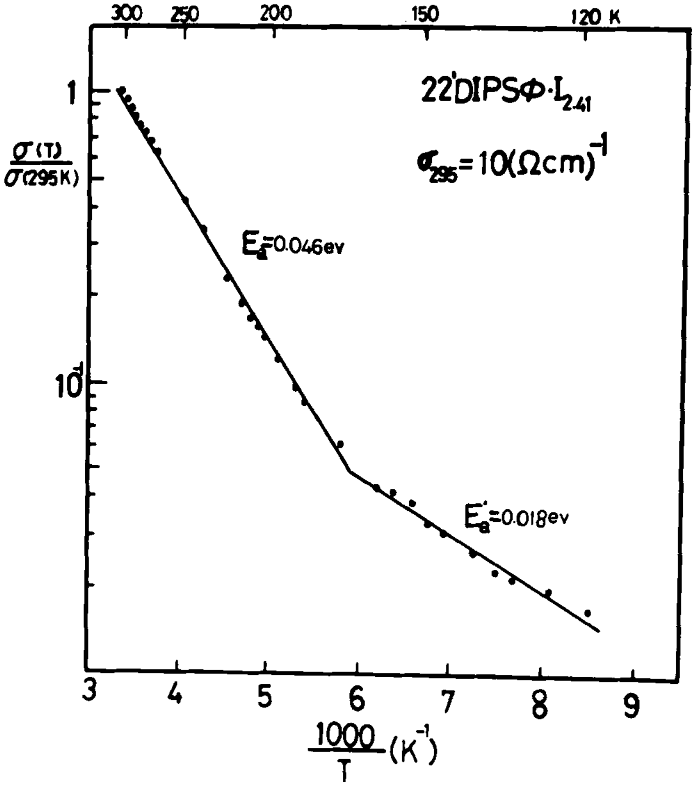


FIGURE 1. The temperature dependence of conductivity of 2,2'DIPSØ$_4$I$_{2.41}$.

Single crystals of 2,2'DIPSØ$_4$ showed a conductivity of 10^{-11} (ohm cm)$^{-1}$ along the needle axis. However, single crystal of 2,2'DIPSØ$_4$I$_{2.41}$ showed high conductivity 10 (ohm cm)$^{-1}$ along the needle axis at room temperature using d.c. four-probe method of conductivity measurement. The temperature dependence of conductivity (FIGURE 1) followed the following relation

$$\sigma(T) = \sigma_0 \exp(-E/KT)$$

with two different activation energies of 0.046ev between room temperature and 170K and 0.018ev at lower temperatures.

The specific conductivities of 1:1 and 1:2 TCNQ complexes measured on rectangular bars of powder compaction (700Kg/cm^2) were 0.9 (Ohm cm)$^{-1}$ and 0.2 (ohm cm)$^{-1}$ respectively at room temperature. Voltage-shorted compaction (VSC)[3] conductivity measurements on 1:1 TCNQ complex showed a broad maximum around 223K, the 1:2 TCNQ complex showed a sharp maximum around 273K (FIGURE 2). Single crystal of these complexes are clearly

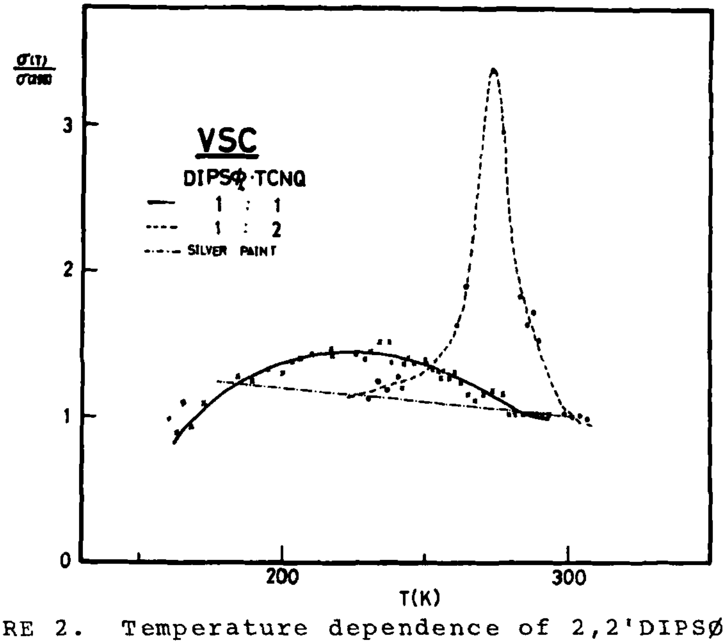


FIGURE 2. Temperature dependence of 2,2'DIPSØ$_4$-TCNQ, 2,2'DIPSØ$_4$TCNQ$_2$ voltage-shorted conductivity

needed and continued attempts are in progress.

THE ELECTRONIC SPECTRA OF TCNQ COMPLEXES

The electronic absorption spectra of TCNQ charge transfer complexes of high conductivity show characteristic absorption peaks A and B below 1.5ev [4-8]. The absorption spectra of 2,2'DIPSØ$_4$ and it's TCNQ complexes were measured in KBr pressed disks (FIGURE 3) to show the absorption peak A at 0.64ev and 0.7ev for 1:1, 1:2 TCNQ complexes respectively and the absorption peak at 1.42ev for both complexes. These are believed to be a mixed valence transition for high conductivity.

The degree of charge transfer, ρ, from donor to TCNQ has an important influence on both the conductivity and optical absorption properties. We have measured the S_{2p}, N_{1s} binding energies for sulfur and nitrogen in 2,2'DIPSØ$_4$,TCNQ,LiTCNQ,2,2' DIPSØ$_4$ClO$_4$,2,2'DIPSØ$_4$TCNQ,2,2'DIPSØ$_4$TCNQ$_2$ by X-ray photoelectron spectroscopy (XPS) from which the degree of charge transfer between 2,2'DIPSØ$_4$ and

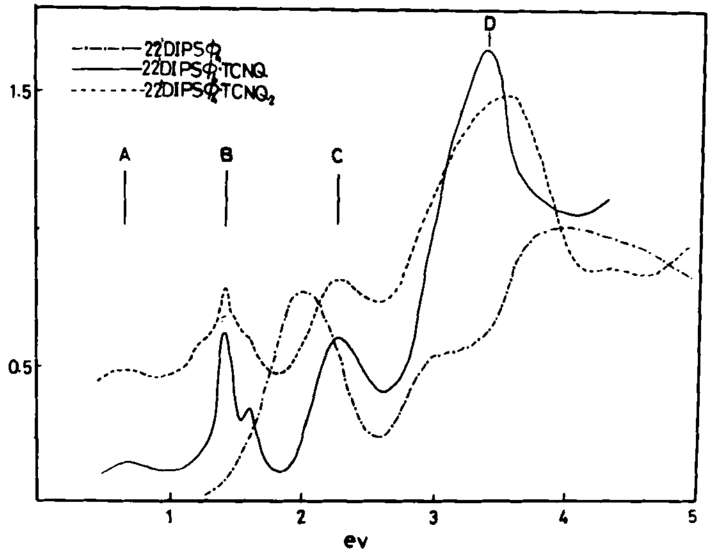


FIGURE 3. The electronic spectra of 2,2'DIPSØ$_4$ and it's TCNQ complexes.

TCNQ to be $\rho=0.4$ and 0.9 for 1:1 and 1:2 TCNQ complexes respectively [9]. These results confirmed the incomplete charge transfer present in both TCNQ complexes.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the assistance of Mr. Zhang Ming-qian and the research groups of Mass spectrometry and elemental analysis.

REFERENCES

1. S.Hunig, B.J.Garner, G.Ruider and W.Schenk Liebigs Ann. Chem., 1036 (1973).
2. P.Calas, J.M.Faber, E.Torreilles and L.Giral C.R.Acad.Sci., 280, 901 (1975).
3. L.B.Coleman, Rev.Sci.Instr., 49, 58 (1978).
4. J.B.Torrance, Coference of Organic Conductors and Semiconductors (Siofok Hungray 1976) p.453-467.
5. J.Tanaka, M.Tanaka, T.Kawai, T.Takabe and O.Maki, Bull.Chem.Soc.Japan, 49, 2358 (1976).
6. J.B.Torrance, B.A.Scott and F.B.Kaufman, Solid State Commun., 17, 1369 (1975).
7. H.Strazlecka and W.Schoenfelder, Mol.Cryst.Liq. Cryst., 52, 307 (1979).
8. J.B.Torrance, Accounts of Chemical Research, 12, 79-86 (1979).
9. Chao Liangzhong, Lin Shihung, Zhu Daoben and QianRenyuan, to be published.