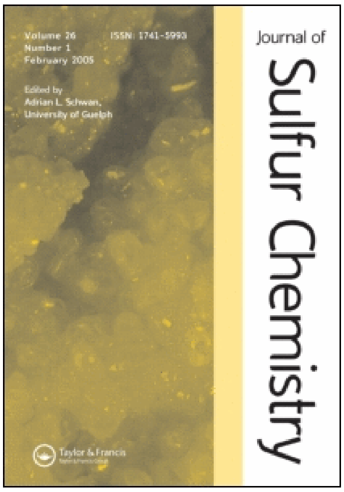

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Organic Conductors - Synthesis and Physical Properties of 4:4'-Bi(pyranylidenes) and Bi(chalcogenopyranylidenes): Charge Transfer Complexes and Radical Ion Salts

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Organic Conductors - Synthesis and Physical Properties of 4:4′-Bi(pyranylidenes) and Bi(chalcogenopyranylidenes): Charge Transfer Complexes and Radical Ion Salts

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This review describes the synthesis of electron π donors in the 4:4′-bi(pyranylidenes), 4:4′-bi(thiopyranylidenes), 2:2′-bi(thiopyranylidenes), 4:4′-bi(selenopyranylidenes), 4:4′-bi(telluropyranylidenes) series symmetrically substituted at the α,α′-positions of the heteroatom. Some selected properties of these compounds are included (oxidation potentials, spectroscopic data, crystal structures) and the optical, magnetic and electrical characteristics of the charge transfer complexes and radical ion salts derived from these electron donors have been collected and are discussed.

Key words: 4:4′-Bi(pyranylidenes), 4:4′-bi(chalcogenopyranylidenes), charge transfer complexes, radical ion salts, synthesis, crystal structures, optical spectra, magnetic susceptibility, electrical conductivity, oxidation potentials, electron donors, liquid crystals, mesomorphism.

CONTENTS

1. INTRODUCTION

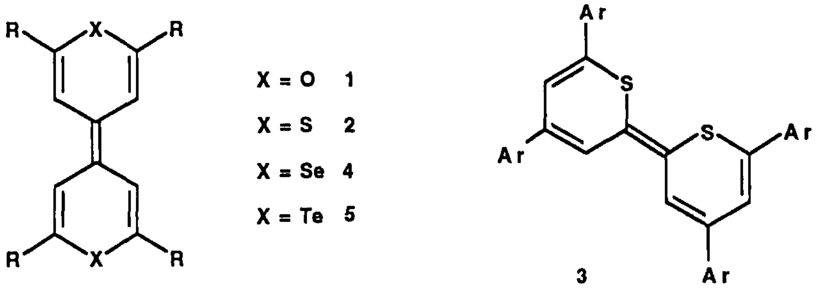
Since the discovery of the quasi-monodimensional conducting character of the charge transfer complex of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), considerable work has been carried out on the synthesis of electron donors derived from TTF[1] as with similar structures[2] and their complexes. Some authors[2–7] have attempted to correlate the more or less average metallic properties of such complexes with the structure and the molecular characteristics of the donor. The result is that some particular conditions seem necessary to obtain on organic metal. Among others are:

—Planarity of the electron donor structure[3] with, in most of the cases, one or several chalcogens which induce an intrachain overlap due to the large spatial extension of the orbitals;[4]

—Increase in aromaticity resulting from the formation of an electron sextet by the loss of electrons during charge transfer.[2] This condition has, however, been disputed;[8]

—Partial degree of charge transfer (ρ) between the donor and the acceptor; so as to obtain a mixed valence system ($\rho \neq 1$). This implies for the TCNQ complexes that the donor's first oxidation potential is relatively low, generally lower than 0.6 V/ECS. Moreover, several relations[5,6,7] have been proposed between the oxidation potential of the donor, $E_1(D)$, and the reduction potential of the acceptor, $E_1(A)$, in order to obtain a mixed valence system. Thus, for example, Saïto and Ferraris[6] suggest the following relation: $-0.02\ \mathrm{V} \leq E_1(D) - E_1(A) \leq 0.34\ \mathrm{V}$.

These studies have led many authors [cf. ref. 9 and references cited therein] to synthesize electron donors in the bi(chalcogenopyranylidene) series, isoelectronic with the tetrachalcogenafulvalenes. These heterocycles derived from chalcogenopyranes satisfy the previous criteria: planarity, increase in aromaticity by loss of an electron and suitable oxidation potential. It was of interest therefore to review the synthesis, the structure and the physical properties of 4:4'-bi(pyranylidenes), 4:4'-bi(chalcogenopyranylidenes), 2:2'-bi(thiopyranylidenes) and their substituted derivatives, as well as their charge transfer complexes and their radical ion salts.



R = H **a**; CH_3 **b**; $COOC_2H_5$ **c**; *t*-Bu **d**; SCH_3 **e**; C_6H_5 **f**; *p*-$CH_3C_6H_4$ **g**; *p*-$CH_3OC_6H_4$ **h**; *p*-$CH_3SC_6H_4$ **i**; *p*-FC_6H_4 **j**; *p*-ClC_6H_4 **k**; 2-thienyl **l**; *p*-$C_8H_{17}C_6H_4$ **m**; *p*-$C_9H_{19}C_6H_4$ **n**; *p*-$C_{12}H_{25}C_6H_4$ **p**.

SCHEME 1

1. SYNTHESIS OF DONORS

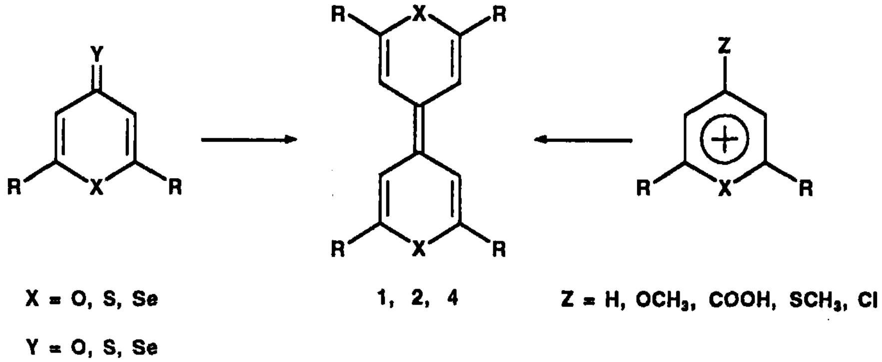
1.1. *4:4'-Bi(pyranylidenes)* 1

We observe that research on organic conductors with donors having isoelectronic structures of the TTF system started by obtaining charge transfer complexes built from 4:4'-bi(pyranylidenes):[10,11] the synthesis of some of these donors was already known [cf. ref. 12 and references cited therein, e.g.,[13]]. The synthesis of 4:4'-bi(pyranylidenes) symmetrically substituted at the α,α'-positions relative to the oxygen is carried out starting from:

—4*H*-pyran-4-ones, by reductive coupling[14,15]

—4*H*-pyran-4-thiones and 4-selenones, by heating under various conditions,[12,13,14,16,25] by electrochemical coupling[17] and by photolysis[18,19]

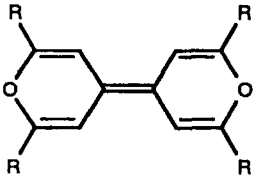
—Substituted pyrylium ions,[14,20–24] if the reduction is carried out with zinc (Z = H), it gives sometimes a dihydro derivative as intermediate which is oxidized *in situ* by the pyrylium ion.[20]



SCHEME 2

The photodimerisation of the 2,6-diphenylpyrylium ion has also been studied.[26] Coupling by electrochemical reduction of 2,6-diarylpyrylium ions leads to the corresponding 4:4'-bi-(pyranylidenes).[27]

TABLE 1 Symmetrically substituted 4:4'-bi(pyranylidenes) **1**

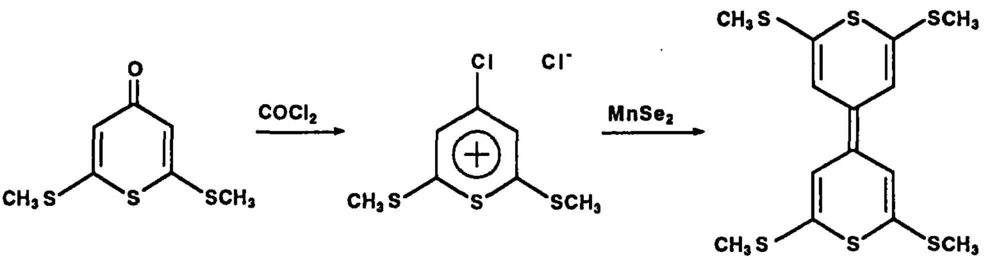


	R	m.p. °C	References
1a	H	170 dec.	14, *15*
1b	CH_3	184–186	10, 14, *16*, 17
1c	$COOC_2H_5$	201–203	*28*
1f	C_6H_5	313 320–323	11, 12, *13*, *14*, 17, 18, 20, 21, 22, 23, 24, 27, 28, 29
1g	p-$CH_3C_6H_4$	351–355	*11*, 20
1h	p-$CH_3OC_6H_4$	291–292	*11*, 13, 17, 20, 23
1l	(2-thienyl)	344–346	*11*, 17, 20
1m	p-$C_8H_{17}C_6H_4$	mesogen	31
1n	p-$C_9H_{19}C_6H_4$	mesogen	31
1p	p-$C_{12}H_{25}C_6H_4$	mesogen	17, 30, 31
11	o-$C_nH_{2n+1}OC_6H_4$ (n = 7,8,9,12)	mesogen	31
12	m-$C_nH_{2n+1}OC_6H_4$ (n = 7,8,9,12)	mesogen	31
13	p-$C_nH_{2n+1}OC_6H_4$ (n = 7,9,12)	mesogen	31
14	3,4-$(C_nH_{2n+1}O)_2C_6H_3$ (n = 1,4,10)	mesogen	27

References in italics correspond to m.p. °C.

1.2. *4:4'-Bi(thiopyranylidenes)* **2**

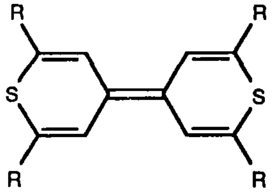
The synthesis of 4:4'-bi(thiopyranylidenes) **2** has been carried out, in the majority of the cases, according to the process shown in Scheme 2, starting from thiopyran-4-thiones under various conditions.[14,18,29,32] The 4:4′-bi(thiopyranylidenes) are obtained by reductive duplication of the corresponding thiopyrylium ions, either by zinc[31] or by activated zinc in acetonitrile.[33] In the case where R = phenyl, **2f** can also be obtained by treatment of the thiopyrylium ion with triphenylphosphine in pyridine.[22] The 4:4′-bi(2,6-dimethylthio-thiopyranylidene) **2e** is obtained from 4-chloro-2,6-dimethylthio-thiopyrylium chloride by reaction with manganese diselenide.[33]



2e

SCHEME 3

TABLE 2 Symmetrically substituted 4:4′-bi(thiopyranylidenes) **2**



	R	m.p. °C	References
2a	H	150 dec.	*14*
2b	CH_3	218	14, *29*
2c	$COOC_2H_5$	260–263	*28*
2d	*t*-Bu	257–258	32
2e	SCH_3	115	*33*
2f	C_6H_5	322–324	*14*, 18, 22, 24, 34
2g	*p*-$CH_3C_6H_4$	306	*33*
2h	*p*-$CH_3OC_6H_4$	250	*96*
2j	*p*-FC_6H_4	158	*33*
2k	*p*-ClC_6H_4	298	*33*
2n	*p*-$C_9H_{19}C_6H_4$	mesogen	31
2p	*p*-$C_{12}H_{25}C_6H_4$	mesogen	31
23	*p*-$C_nH_{2n+1}OC_6H_4$ (n = 9,12)	mesogen	31

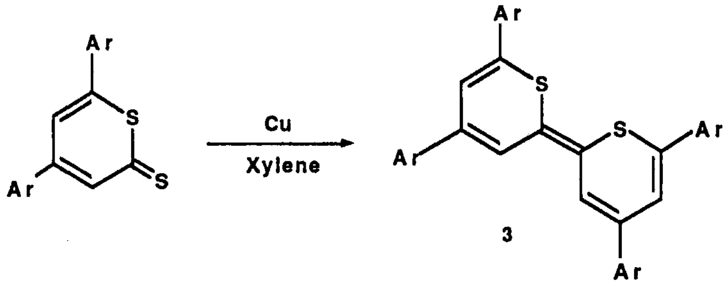
References in italics correspond to m.p. °C.

The 4:4′-bi(2,6-diethoxycarbonyl-thiopyranylidene) **2c** is obtained in a one step synthesis by treatment of diethyl 2,4,6-trioxoheptanedioate with hydrogen sulfide and hydrogen chloride under pressure (60% yield).[28]

1.3. *2:2′-Bi(thiopyranylidenes)* **3**

The 2:2′-bi(thiopyranylidenes) **3** are obtained by duplication of the corresponding thiopyran-2-thiones[35] by the action of copper in boiling xylene.[33]

The formation of a single *Z*-isomer is observed by comparison of the experimental and calculated dipole moments [**3f**, $\mu_{ex.} = 1.8 \pm 0.2$ D, $\mu_{calc.} = 1.6 \pm 0.5$ D[33]]. The NMR spectra also confirm this structure.[33]



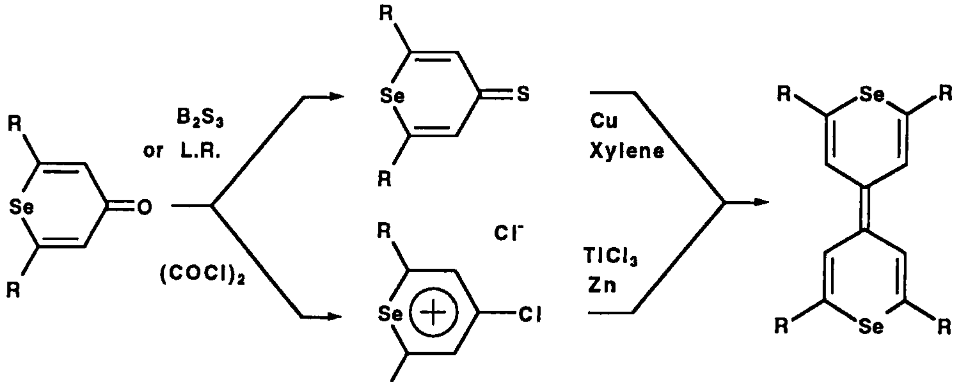
3f	Ar = C_6H_5	m.p. = 257 °C	(33, 36)
3g	Ar = p-$CH_3C_6H_4$	m.p. = 248 °C	(33)
3k	Ar = p-ClC_6H_4	m.p. = 323 °C	(33)

SCHEME 4

1.4. *4:4′-Bi(selenopyranylidenes)* **4**

Two ways of synthesis are used to prepare 4:4′-bi(selenopyranylidenes) **4**,[33,37–39] starting from either selenopyran-4-thiones or from selenopyrylium ions.

Selenopyran-4-thiones are obtained by reflux of the corresponding ketones with boron trisulfide[33,39] or with Lawesson's reagent in hot toluene.[32] The duplication of these thiones which leads to **4** is carried out with powdered copper in boiling toluene or xylene.[32,33,39] 2,6-Diphenyl-1-selenopyran-4-one can also be converted to the corresponding 4-chloroselenopyrylium chloride by the action of oxalyl chloride in toluene with a yield of 90%. The coupling of this selenopyrylium ion is realized by zinc or titanium (III) chloride and leads to 4:4′-bi(2,6-diphenyl-1-selenopyranylidene) **4f** in a yield of 40%.[33]

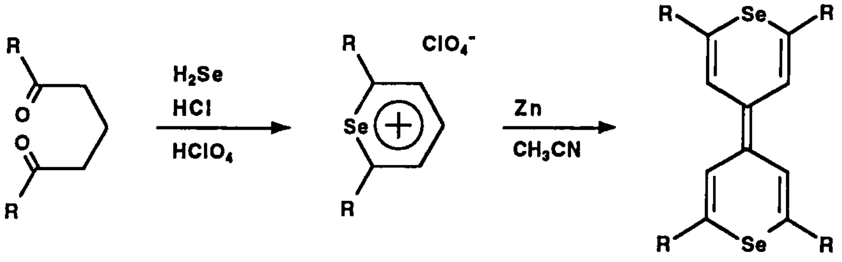


4

L.R.: Lawesson's Reagent [32,40]

SCHEME 5

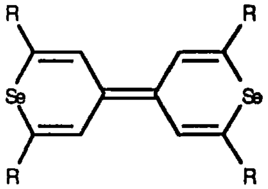
The heterocyclisation of pentane-1,5-diones with hydrogen selenide in the presence of hydrogen chloride in acetic acid leads to selenopyrylium chlorides which are stabilized by anion exchange with perchloric acid. The reduction of selenopyrylium perchlorates with activated zinc gives 4:4′-bi(selenopyranylidenes) in yields between 50 and 90%.[33,39]



4

SCHEME 6

TABLE 3 Symmetrically substituted 4:4'-bi(selenopyranylidenes) **4**

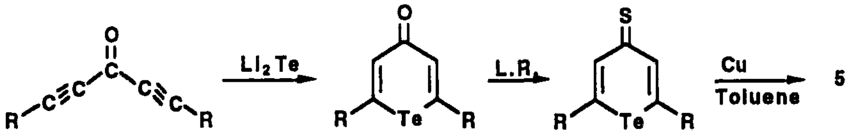


	R	m.p. °C	References
4b	CH_3	214	32, 33, 37, *39*
4d	*t*-Bu	260–263	*32*, 46
4f	C_6H_5	315	32, 33, 37, *39*
4g	*p*-$CH_3C_6H_4$	306	*39*
4h	*p*-$CH_3OC_6H_4$	269	*39*
4i	*p*-$CH_3SC_6H_4$	267	*39*
4k	*p*-ClC_6H_4	344	*39*
4n	*p*-$C_9H_{19}C_6H_4$	mesogen	94
4p	*p*-$C_{12}H_{25}C_6H_4$	mesogen	94
43	*p*-$C_nH_{2n+1}OC_6H_4$ (n = 9,12)	mesogen	94
44	*p*-$C_{12}H_{25}SC_6H_4$	mesogen	94

References in italics correspond to m.p. °C.

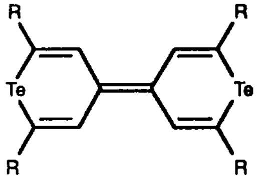
1.5. *4:4'-Bi(telluropyranylidenes)* **5**

These donors are obtained from telluropyran-4-ones, which in turn are obtained by the action of lithium telluride in a strong basic medium on di-1-alkynyl ketones. The strongly basic medium avoids the competing "anti-Michael" addition reaction which leads to a tellurophene derivative.[41] The action of Lawesson's reagent[40] on these telluropyranones in toluene leads to the corresponding thioketones which give, by reaction with powdered copper in toluene, 4:4'-bi(telluropyranylidenes) (Table 4) with yields from 6 to 42%, calculated from the di-1-alkynyl ketones.



SCHEME 7

TABLE 4 4:4′-Bi(telluropyranylidenes) **5**



	R	m.p. °C	References
5b	CH_3	212–217 dec.	*32*, 41
5d	*t*-Bu	273–275	*32*, 41
5f	C_6H_5	273–274	*32*, 41
5g	*p*-$CH_3C_6H_4$	280–290 dec.	*39*

References in italics correspond to m.p. °C.

2. PROPERTIES OF 4:4′-BI(PYRANYLIDENES) AND 4:4′-BI(CHALCOGENO-PYRANYLIDENES)

2.1. *Crystal and Electronic Structures*

The crystal structures of 4:4′-bi(2,6-diphenylpyranylidene)[42] and 4:4′-bi(2,6-diphenyl-1-chalcogenopyranylidenes) [X = S,[43] X = Se,[44] Fig. 1] and of 4:4′-bi(2,6-diethoxycarbonyl-1-thiopyranylidene)[45] have been determined. The C-X bound length (X = O, S, Se) increases with the atomic number of X.

The length of the central bond C(4)-C(4′) remains about 1.40 Å midway between a single and a double bond. The bonds C(2)-C(3) and C(5)-C(6) possess pure double bond character (d = 1.33 Å).

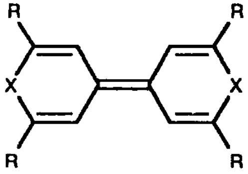
The heterocyclic system is approximately planar, with a slight folding along the X—C(4) axis which increases from X = O to X = Se. This folding gives, for example, the selenopyrane heterocycle a boat conformation where Se and C(4) are at 0.15 Å and 0.11 Å, respectively, above the average plane formed by the other ring atoms. With X = O and X = S this deformation is weaker [X = S (0.13 and 0.09 Å); X = O (0.045 Å and 0.021 Å)]. We also noticed that in the crystal the molecules arrange themselves into columns along the b axis (X = S and X = Se), (Fig. 1).

The electronic structure of the donors **1** to **4** (**a**, **b**, **f**) has been studied by theoretical chemistry methods with parametrization and related to photoelectron spectra.[47] In particular, the electronic structure of **2f** has been calculated by means of a "multiple scattering X_α method": the results led to the interpretation of its X-ray photoelectron spectrum.[48,49]

2.2. *Electrochemical Behaviour*

The oxidation potentials of the 4:4′-bi(pyranylidenes) **1** and the bi(chalcogenopyranylidenes) **2** to **5** (Tables **5** and **6**) show that these heterocycles are

TABLE 5 Oxidation potentials of 4:4′-bi(pyranylidenes) and 4:4′-bi(chalcogenopyranylidenes)



	X	R	Electrode	Solvent	Electrolyte	E_1	E_2	Reference and measurement method	
1a	O	H	Ag/AgCl	CH_3CN	$TBABF_4$	0.21	0.50	14	A
1b	O	CH_3	Ag/AgCl	CH_3CN	$TBABF_4$	0.03	0.42	14	A
1b	O	CH_3	ECS	CH_2Cl_2	$TBABF_4$	0.04	0.42	32	B
1d	O	*t*-Bu	ECS	CH_2Cl_2	$TBABF_4$	0.10	0.53	32	B
1f	O	C_6H_5	Ag/AgCl	CH_3CN	$TBABF_4$	0.15	0.47	14	A
1f	O	C_6H_4	ECS	CH_2Cl_2	$TBABF_4$	0.15	0.47	32	B
1f	O	C_6H_5	ECS	CH_2Cl_2	$TBABF_4$	0.22	0.68	31	C
1f	O	C_6H_5	ECS	CH_3CN	$TBABF_4$	0.25	0.72	27	C
1h	O *	*p*-$CH_3OC_6H_4$	ECS	CH_2Cl_2	$TBABF_4$	0.02	—	31	C
2a	S	H	Ag/AgCl	CH_3CN	$TBABF_4$	0.20	0.46	14	A
2b	S	CH_3	Ag/AgCl	CH_3CN	$TBABF_4$	0.09	0.34	14	A
2b	S	CH_3	ECS	CH_2Cl_2	$TBABF_4$	0.08	0.34	32	B
2d	S	*t*-Bu	ECS	CH_2Cl_2	$TBABF_4$	0.11	0.37	32	B
2e	S	CH_3S	ECS	$CH_2C1CHCl_2$	TEAT	$E_{1/2}$ = 0.43		33	A
2f	S	C_6H_5	Ag/AgCl	CH_3CN	$TBABF_4$	0.22	0.41	14	A
2f	S	C_6H_5	ECS	CH_2Cl_2	$TBABF_4$	0.22	0.41	32	B
2f	S	C_6H_5	ECS	CH_2Cl_2	$TBABF_4$	0.33	0.55	31	C
2g	S	*p*-$CH_3C_6H_4$	ECS	$CH_2ClCHCl_2$	TEAT	0.23	0.39	50	A
2g	S	*p*-$CH_3C_6H_4$	ECS	DMF	TEAT	0.17	0.29	33	A
2h	S	*p*-$CH_3OC_6H_4$	ECS	CH_2Cl_2	$TBABF_4$	0.21	0.45	31	C
2j	S	*p*-FC_6H_4	ECS	$CH_2ClCHCl_2$	TEAT	0.28	0.37	33	A

2k	S *	p-ClC_6H_4	ECS	$CH_2ClCHCl_2$	TEAT	0.34	0.44	33	A
4b	Se	CH_3	ECS	CH_2Cl_2	$TBABF_4$	0.12	0.29	32	B
4b	Se	CH_3	ECS	CH_3CN	TEAT	0.13	0.29	50	A
4b	Se	CH_3	ECS	$CH_2ClCHCl_2$	TEAT	0.17	0.39	39	A
4d	Se	t-Bu	ECS	CH_2Cl_2	$TBABF_4$	0.20	0.44	32	B
4f	Se	C_6H_5	ECS	CH_2Cl_2	$TBABF_4$	0.33	0.48	32	B
4f	Se	C_6H_5	ECS	$CH_2ClCHCl_2$	TBAP	0.34	0.53	39	A
4g	Se	p-$CH_3C_6H_4$	ECS	$CH_2ClCHCl_2$	TEAT	0.23	0.39	39	A
4h	Se	p-$CH_3OC_6H_4$	ECS	$CH_2ClCHCl_2$	TEAT	0.18	0.30	39	A
4i	Se	p-$CH_3SC_6H_4$	ECS	$CH_2ClCHCl_2$	TEAT	0.28	0.35	39	A
4k	Se *	p-ClC_6H_4	ECS	$CH_2ClCHCl_2$	TEAT	$E_{1/2}$ = 0.44		39	A
5b	Te	CH_3	ECS	CH_2Cl_2	$TBABF_4$	0.22	0.36	32	B
5d	Te	t-Bu	ECS	CH_2Cl_2	$TBABF_4$	0.24	0.38	32	B
5f	Te	C_6H_5	ECS	CH_2Cl_2	$TBABF_4$	0.34	0.49	32, 41	B
5g	Te	p-$CH_3C_6H_4$	ECS	CH_3CN	TEAT	0.20	0.27	39	A

TBAP: Tetrabutylammonium perchlorate
TBABF$_4$: Tetrabutylammonium tetrafluoroborate
TEAT: Tetraethylammonium tosylate
Measured by:
A: polarography
B: cyclic voltammetry with glassy carbon electrode
C: cyclic voltammetry with Pt electrode

* The oxidation potentials of 4:4′-bi(2,6-diphenylpyranylidenes) and 4:4′-(2,6-diphenyl-1-thiopyranylidenes) with long alkyl chains on the aryl groups: C_nH_{2n+1} [**1m, 1n,1p, 2n, 2p**] and OC_nH_{2n+1} [**11, 12, 13, 14, 23**] are listed in references.[27,31] The oxidation potentials of 4:4′-Bi(2,6-diphenyl-1-selenopyranylidenes) with long alkyl chains on the aryl groups: C_nH_{2n+1} [**4n, 4p**], OC_nH_{2n+1} [**43**] and $SC_{12}H_{25}$ [**44**] are listed in references.[50,94]

TABLE 6 Oxidation potentials of 2:2′bi-4,6-diaryl-1-thiopyranylidenes)

	Ar	Electrode	Solvent	Electrolyte	E_1	E_2	Ref.
3f	C_6H_5	ECS	$CHCl_2CH_2Cl$	TEAT	0.27	0.42	33
					0.23	0.39	36
3g	p-$CH_3C_6H_4$	ECS	$CHCl_2CH_2Cl$	TEAT	0.20	0.37	33
3k	p-ClC_6H_4	ECS	$CHCl_2CH_2Cl$	TEAT	0.31	0.41	33

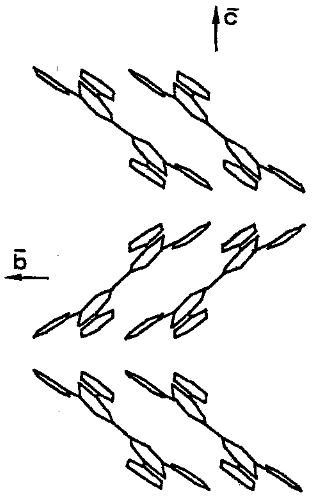
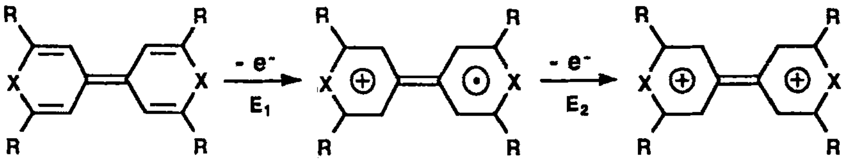


FIGURE 1 Projection of **4f** along the a axis. *Reprinted by permission from ref. 39.*

good electron donors. In most cases this oxidation involves two distinct steps, with the formation of a radical cation as the first step.



SCHEME 8

The oxidation potentials are very close to those of the tetrachalcogenafulvalene series,[1] in particular the first potentials of donors **1** to **5** generally correspond to the criteria of Torrance[5] and Saito *et al.*[6] for conducting complexes with TCNQ. One can equally note that an increase in the size of the heteroatom leads to an increase in the first oxidation potential due to the weaker overlapping of the heteroatom orbitals with the ring carbons' 2p π orbitals.[32] On the other hand, the difference between the two oxidation potentials decreases with a roughly linear behaviour with decreasing ionisation potential of the heteroatom[50] (Fig. 2).

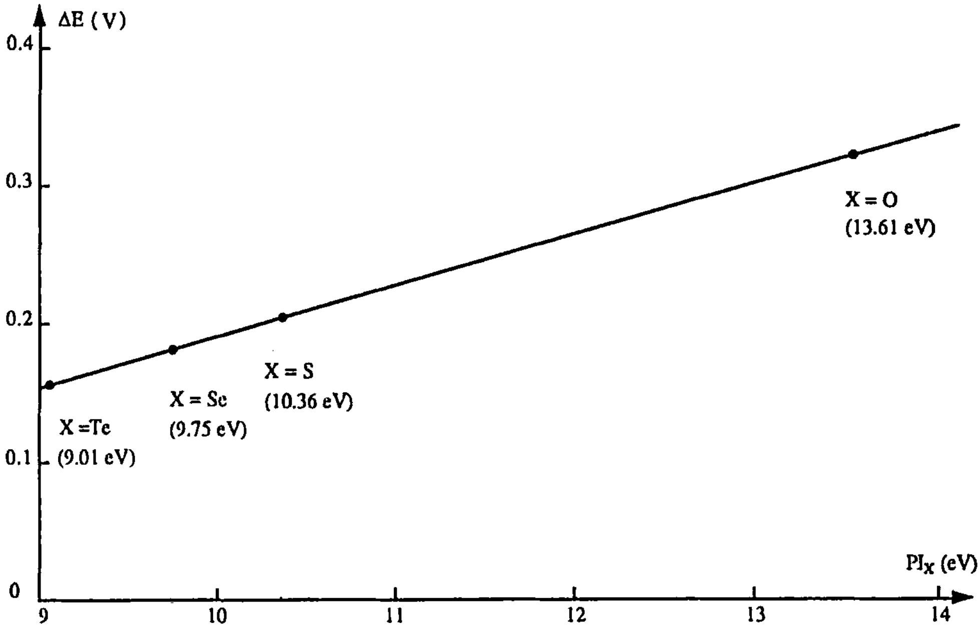


FIGURE 2 Relation between ΔE and PI$_x$.[50] ΔE: Difference between the oxidation potentials of the donors **1f**, **2f**, **4f**, and **5f**. PI$_x$: Ionisation potentials of the heteroatoms O, S, Se, Te.

The nature of the R substituent has an equally important influence, the substitution of methyl by phenyl leads to an increase of the first oxidation potential from 0.10 to 0.17 V depending on the nature of X (Table 5). A near linear relationship has been established between the first oxidation potential of 4:4′-bi(2,6-diaryl-1-selenopyranylidenes), **4f**, **4g**, **4h**, **4i** and **4k** and the electronic effect of the phenyl para substituent characterized by its Hammett constant[50] (Fig. 3).

2.3. *Spectral Characteristics*

An ESR study on radical cations generated from 4:4′-bi(2,6-di-*t*-butyl-pyranylidene) **1d** and the 4:4′-bi(2,6-di-*t*-butyl-1-chalcogenopyranylidenes) **2d**, **4d** and **5d** by electrochemistry shows that the electronic densities are similar on the carbon ring and on the heteroatom, whatever its nature.[32]

The electronic spectra[14,39,41] of these donors display especially an absorption maximum at high wavelength in the region 450–520 nm when R = phenyl. A bathochromic effect is observed when X varies from O to Te, depending on the nature of the substiuent [R = alkyl and R = aryl]. The electronic and infrared spectra of the donor **2f** and its iodide salts have been recently analyzed,[51] especially as a function of the temperature.

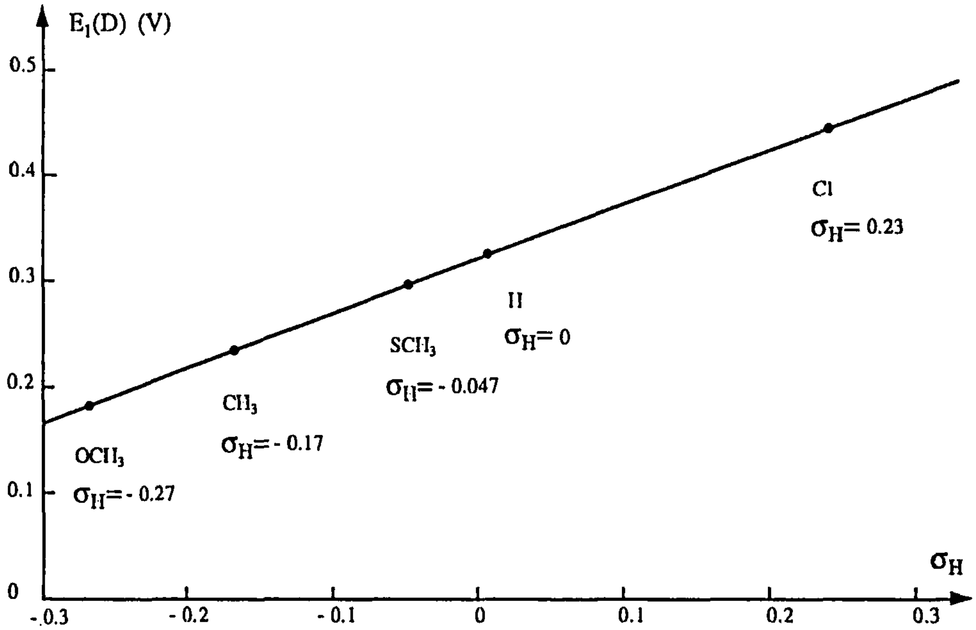


FIGURE 3 Relation between $E_1(D)$ and σ_H[50] $E_1(D)$: First oxidation potential of the donors **4f**, **4g**, **4h**, **4i**, **4k** with R = p-C_6H_4R'; σ_H = Hammett constant for R' = H, CH_3, CH_3O, CH_3S, Cl.

The mass spectra of the 4:4'-bi(chalcogenopyranylidenes) **4** and **5** have been determined;[39,52] ion fragments corresponding mainly to the loss of one heteroatom (X = Se) and for X = Te, the successive loss of two heteroatoms is observed.

3. CHARGE TRANSFER COMPLEXES FROM:

3.1. *4:4'-Bi(pyranylidenes)* 1

Complexes of the stoichiometry 1:1 between donors **1** and different acceptors, Table 7, are generally obtained by mixing of equimolecular quantities of the donor and the acceptor in acetonitrile or methylene chloride.[11] Conductivity values of the compacted powders and more precisely studies of the variation of the conductivity of a monocrystal as a function of temperature for the complex **1f**-TCNQ shows that they are semiconductors [E_a = 0.04 eV for **1f**-TCNQ].[53]

Optical absorption and reflectance spectra have been determined for the **1f**-TCNQ complex; they confirm its semiconductor character with low-energy interband transitions.[54] The magnetic properties of some complexes have also been studied.[11,53,55] Some proton-spin lattice relaxation measurements of the **1f**-TCNQ complex show that the electrons have a localised behaviour below 200 K and a delocalised one at higher temperatures.[56,57] Electronic and IR spectra of some **1f** complexes have been determined and interpreted.[58]

TABLE 7 Charge transfer complexes from 4:4′-bi(pyranylidenes) **1**

	R	Acceptor and stoichiometry D/A		Conductivity $\sigma_{r.t.}$ S cm^{-1}	References
1a	H	TCNQ	1/1	6×10^{-2}	11
1b	CH_3	HCNB	1/1	2×10^{-2}	10, 55
1b	CH_3	DDQ	1/1	—	10
1b	CH_3	TCNQ	1/1	10^{-7}	11
1b	CH_3	TCNQ	1/1	10^{-16}	10
1f	C_6H_5	TCNQ	1/1	1.7	11
1f	C_6H_5	TCNQ	1/1	25–40*	53
1g	p-$CH_3C_6H_4$	TCNQ	1/1	10^{-1}	11
1h	p-$CH_3OC_6H_4$	TCNQ	1/1	2.5×10^{-4}	11
1l	2-thienyl	TCNQ	1/1	10^{-6}	54

HCNB: Hexacyanobenzene, DDQ: dichlorodicyano-*p*-benzoquinone.
The conductivities were measured on compacted powders except for **1f**-TCNQ; *(single crystal).

3.2. *4:4′-Bi(thiopyranylidenes)* **2**.

3.2.1. *Synthesis and Structure.* The complexes are generally obtained by mixing of solutions of the donors **2** with the acceptor in various solvents (acetonitrile, dichloromethane, *N*,*N*-dimethylformamide) in an inert atmosphere. The techniques used, in particular for obtaining single crystals, have been described by several authors.[33,59,60] The complexes and their electrical conductivities are listed in Table **8**.

TABLE 8 Charge transfer complexes from 4:4′-bi(thiopyranylidenes) **2**

	R	Acceptor and stoichiometry D/A		Conductivity $\sigma_{r.t.}$ S cm^{-1}	References
2a	H	TCNQ	1/1	1–30*	25, 59
2a	H	TCNQ	1/2	8	25
2a	H	TCNQ	2/3	0.05–0.1	59
2b	CH_3	TCNQ	1/1	10^{-4}–10^{-3}*	25
2b	CH_3	TCNQ	1/2	0.5	25
2b	CH_3	TCNQ	1/1	10^{-4}	10
2b	CH_3	HCNB	1/1	10^{-4}*	10, 55
2b	CH_3	DDQ	—	10^{-10}	10
2e	CH_3S	TCNQ	1/1	1.3–8*	33, 62
2f	C_6H_5	TCNQ	1/1	250–300*	53
2g	p-$CH_3C_6H_4$	TCNQ	1/1	0.7	33
2j	p-FC_6H_4	TCNQ	1/1	0.1	33
2k	p-ClC_6H_4	TCNQ	1/1	0.37	33

HCNB: Hexacyanobenzene, DDQ: dichlorodicyano-*p*-benzoquinone.
The conductivities are measured on compacted powders excepted for *(single crystal).

The structure of the 4:4′-bi(thiopyranylidene) **2a** complex with TCNQ of the stoichiometry 2/3 [$(\mathbf{2a})_2(\mathrm{TCNQ})_3$] has been determined.[59] It crystallizes in a triclinic system and includes a mixed stack of a pair of donor **2a** nearly planar and three TCNQ; the average distance in the stacks between the donors and the acceptors is 3.37 Å.

4:4′-Bi(2,6-dimethyl-1-thiopyranylidene)-TCNQ, [**2b**-TCNQ], also crystallizes in a triclinic system and exhibits a mixed stack of one donor molecule, practically planar with the exception of the methyl hydrogens, and one acceptor molecule, with an average distance between the molecular planes of 3.40 Å.[60] The determination of the only lattice parameters has been carried out for the monoclinic crystals of 4:4′-bi(2,6-diphenyl-1-thiopyranylidene)-TCNQ.[53]

3.2.2. *Optical spectra.* Absorption spectra have been determined for complexes of TCNQ with 4:4′-bi(2,6-diphenyl-1-thiopyranylidene)[54] and 4:4′-bi(2,6-dimethythio-1-thiopyranylidene).[33] In the high energy range (30 000–16 000 cm^{-1}) the peaks observed between 24 000 and 26 000 cm^{-1} have been attributed to TCNQ as well as to the dimer of the TCNQ anion radical.[54] Towards 17 000 cm^{-1}, the observed absorption would be mainly due to the donor. In the case of the 4:4′-bi(2,6-dimethylthio-1-thiopyranylidene)-TCNQ, [**2e**-TCNQ], the absorption decreases up to 9 000 cm^{-1}, approximately corresponding to the plasma frequency; then a new peak towards 2 000 cm^{-1} is attributed to an intraband transition assigned as A according to.[64]

The specular reflectance spectrum of the 4:4′-bi(2,6-diphenyl-1-thiopyranylidene)-TCNQ [**2f**-TCNQ] complex has been determined with a compacted powder.[54] The reflectance decreases with increasing energy as for a metal. The plasma frequency according to the reflectance minimum would be at an energy of 0.75 eV. The parametrization of the reflectance curve (component $R/\!/$), according to Drude's model allows to determine the dielectric constant at infinite frequency, ϵ_∞, the plasma frequency ω_p, (expressed in eV as $\hbar\omega$), the relaxation time of the free carriers τ as well as the optical conductivity at zero frequency σ_{opt}.

$$[\epsilon_\infty = 3.05;\ \omega_p = 0.99\ \mathrm{eV};\ \hbar\tau^{-1} = 0.287\ \mathrm{eV};\ \sigma_{opt} = 470\ \mathrm{S\ cm}^{-1}].^{54}$$

3.2.3. *Electrical and magnetic properties.* Most of the conductivities of the complexes of the donors **2** have been measured on compacted microcrystalline powders. The values obtained, at room temperature, are generally lower than for TTF-TCNQ complexes under the same conditions [TTF-TCNQ: $\sigma_{r.t.} = 10$ $\mathrm{S\ cm}^{-1}$].[61] The conductivities of some of the donors **2** with TCNQ and HCNB have been determined on single crystals. The study of the conductivity variation as a function of temperature allows, in an appropriate range, to specify the metallic or semiconducting behaviour.

The complex conductivity of **2a**-TCNQ as a function of temperature ($\sigma_{r.t.} =$ 30 $\mathrm{S\ cm}^{-1}$) is characteristic of a semiconductor with an activation energy of 0.13 eV from ambient temperature to 80 K.[59] The complex $(\mathbf{2a})_2$-$(\mathrm{TCNQ})_3$ is also a semiconductor ($\sigma_{r.t.}$ = 0.10 S cm^{-1}) with an activation energy of 0.16 eV.[59] The **2b**-HCNB complex displays semiconductor character [$\sigma_{r.t.}$ = 10^{-4} S cm^{-1}, σ_{77K} = 10^{-7} S cm^{-1}] with an activation energy of 0.45 eV.[55] The **2f**-TCNQ complex displays a high conductivity ($\sigma_{r.t.}$ = 250–300 S cm^{-1}, single crystal) with a metallic behaviour up to 140 K where it undergoes a metal-semiconductor transition ($\sigma_{max}/\sigma_{r.t.}$ = 1.6).[53,54] In the case of the **2e**-TCNQ complex a conductivity of 8 S cm^{-1} of a single crystal is observed at room temperature, (Fig. 4) (the inaccuracy of the results may be due to the very small dimensions of the crystal). The thermal variation shows a slight maximum towards 220 K, followed by a relatively slow drop in conductivity.[62]

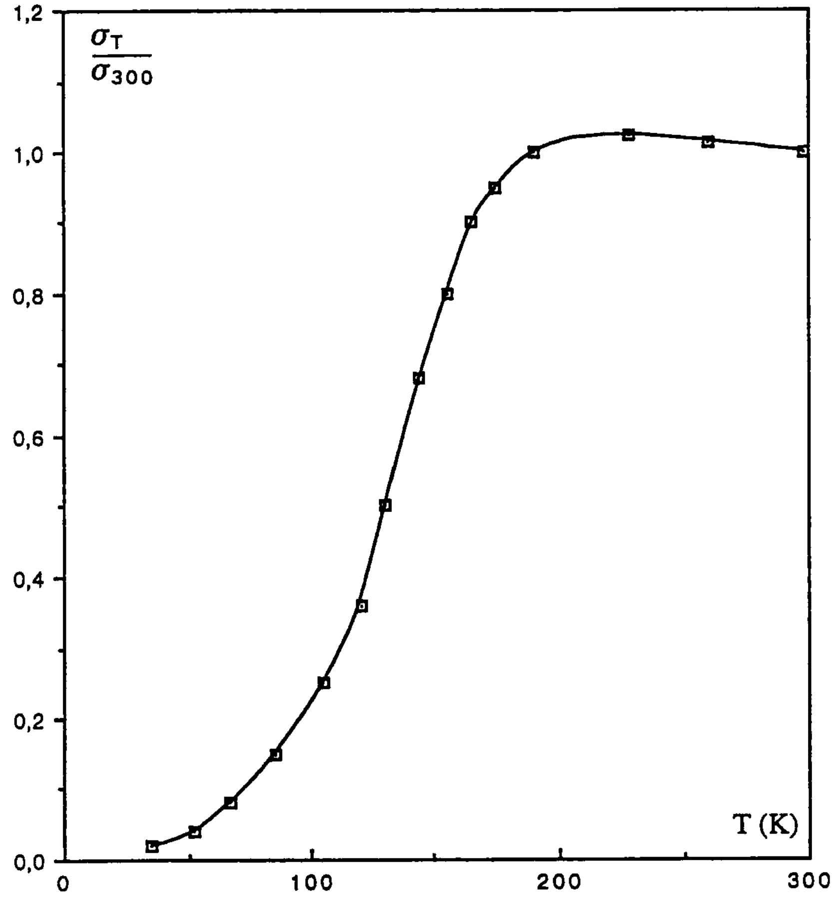


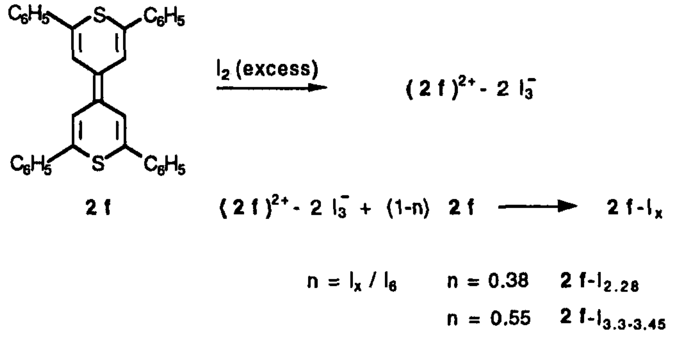
FIGURE 4 Conductivity variation of **2e**-TCNQ (single crystal).[62]

The magnetic susceptibility value of the **2f**-TCNQ complex is 2.1 × 10^{-4} u.e.m./mol at 300 K[63] and decreases linearly with the temperature.[53] Around 47 K, a rise in the susceptibility is observed which is principally attributed to the chemisorbed oxygen.[63] The magnetic susceptibility of the **2b**-HCNB complex is nearly zero and independent of the temperature.[55]

4. RADICAL ION SALTS FROM 4:4′-BI(THIOPYRANYLIDENES) 2

4.1. *Synthesis and Structure*

4:4′-Bi(2,6-diphenyl-1-thiopyranylidene) **2f** forms different radical ion salts upon oxidation with iodine as well as upon disproportionation between a double salt $[(\mathbf{2f})^{2+}, 2\ I_3^-]$ and the neutral donor. The influence of several parameters (concentration of the reagents and their ratios, nature of solvent, temperature) has been studied with the isolation of two radical ion salts: **2f**-$I_{2.28}$ and **2f**-$I_{3.3-3.45}$[65,66] (Scheme 9).



Strzelecka et al.[65]

SCHEME 9

Other authors[67] have obtained by diffusion or slow evaporation of a solution of **2f** and iodine two types of crystals of the stoichiometry **2f**-$I_{2.28}$ (tetragonal) and **2f**-$I_{3.18}$ (orthorhombic). The crystal structure of these ion radical salts has been determined.[67-70] According to these studies[68,69] the tetragonal form includes a regular stack of the donor molecules. The iodide anions, exclusively I_3^- species $[\mathbf{2f}\text{-}(I_3)_{0.76}]$, make up chains which are located in the channels parallel to the columns of donors. The structure of these chains has also been studied by X-ray diffusion as a function of temperature.[71,72] The orthorhombic form of stoichiometry **2f**-$(I_3)_{0.36}$-$(I_5)_{0.40}$ according to ref. [69] consists of I_3^- and I_5^- ions which occupy the channels parallel to the stacks of donors.

4.2. *Optical Properties*

Raman diffusion and absorption spectra of these radical ion salts have been determined.[66,68,73] The **2f**-$I_{2.28}$ salt displays a single intense peak at 107 cm^{-1} in its Raman spectrum due to the I_3^- species while the **2f**-$I_{3.3-3.45}$ salt shows, in addition to this peak, another one at 155 cm^{-1} attributed to the I_5^- species.

The absorption spectra (0.2–5 eV), in the energy range above 1.5 eV, are due essentially to the donor absorptions (neutral and cationic species) and to the iodide anions. In the low energy range we see for the **2f**-$I_{2.28}$ salt a peak centered around 0.3 eV attributed to charge transfer between a radical cation and the neutral donor,[66,68] while the **2f**-$I_{3.3-3.45}$ salt displays a large band around 0.6 eV due to an isovalence transition: $D^{+\cdot} + D^{+\cdot} \xrightarrow{\qquad} D^{2+} + D^{\circ}$.[68]

The specular reflectance spectrum of the **2f**-$I_{2.28}$ salt[66] determined on compacted powder in the range 800–8 000 cm^{-1} displays a plasma edge with a minimum around 4 000 cm^{-1}. The reflectivity data have been analysed with Drude's expression for the dielectric function which leads to the following values: $\epsilon_\infty = 2.8$; $\omega_p = 0.72$ eV; $\hbar/\tau = 0.21$ eV, as well as to the optical conductivity at zero frequency: $\sigma_{opt} = 320$ S cm^{-1}.[66,68]

4.3. *Electrical and Magnetic Properties*

The electrical conductivity of single crystals has been determined for the polyiodides **2f**-$I_{2.28}$ and **2f**-$I_{3.3-3.45}$.[65-67] According to Strzelecka *et al.*[65] the conductivity at room temperature is: $\sigma_{r.t.} = 250$ S cm^{-1} for **2f**-$I_{2.28}$ and $\sigma_{r.t.} = 2$ S cm^{-1} for **2f**-$I_{3.3-3.45}$. The polyiodide **2f**-$I_{2.28}$ would have a metallic behaviour with a maximum conductivity at 220 K and a ratio $\sigma_{max}/\sigma_{r.t.} \approx 1.2$. A detailed study of the conductivity of these polyiodides has also been carried out by Isett *et al.*[67] It shows that the polyiodide **2f**-$I_{2.28}$ has a conductivity along the stacking c axis of $\sigma_{r.t.} = 120$ S cm^{-1} and a maximum conductivity at 220 K with a ratio of $\sigma_{max}/\sigma_{r.t.} \approx 1.13$; we also observe a phase transition at 165 K according to the temperature dependence of the thermoelectric power. The conductivity of this **2f**-$I_{2.28}$ salt is anisotropic with $\sigma_c/\sigma_a \approx 2.5 \times 10^3$. Despite these results and, in particular, the fact that dρ/dT is positive, it does not seem that this material is metallic; the thermoelectric power data suggest a semiconductor state above and below the phase transition at 165 K. The conductivity graph of this polyiodide salt might best be described over a large temperature range by the following type of function, already applied to various TCNQ complexes:

$$\sigma_T/\sigma_{295} = \sigma_0 T^{-\alpha} \times e^{-\Delta/T}$$

with in the case of **2f**-$I_{2.28}$:

$$\alpha = 2.4;\ \Delta = 510 \text{ K } (T > 165 \text{ K})$$

$$\Delta \approx 700 \text{ K } (T < 165 \text{ K})$$

More recently a thorough study of the physical properties of **2f**-$I_{2.28}$ [**2f**-$(I_3)_{0.76}$] single crystals was undertaken.[74] A conductor-semiconductor transition characterized by a large maximum toward 220 K is observed with a conductivity at room temperature of 250 S cm^{-1} [$\sigma_{max}/\sigma_{r.t.}$ = 1.13], and confirms the value already observed by Strzelecka *et al.*[65] The order-disorder phase transitions of the triiodide chain have also been studied by X-ray diffusion as a function of temperature.[74,75] The structural evolution has been linked to the electrical properties of **2f**-$(I_3)_{0.76}$ which displays a Peierls type phase transition around 182 K.[74,76]

The **2f**-$I_{3.18}$ polyiodide salt displays a much weaker conductivity than observed in organic metals, $\sigma_{r.t.}$ = 2 S cm^{-1} along the c axis, with a slight maximum at 250 K [$\sigma_{max}/\sigma_{r.t.} \approx$ 1.05]; no phase transition was noticed.[67]

The magnetic properties of these salts have been particularly studied by magnetic susceptibility and electronic paramagnetic resonance.[77] At very low temperature, as for the **2f**-TCNQ complex, a strong rise in the paramagnetic susceptibility attributed to an absorption of oxygen is observed. In the 100–300 K temperature range, a weak, almost constant, paramagnetism of about 0.2×10^{-4} emu/mol for the polyiodide salt **2f**-$I_{.28}$ and 0.5×10^{-4} emu/mol for the polyiodide salt **2f**-$I_{3.3}$ is observed (Fig. 5). The role of the various iodine chains seems essential for the understanding of the physical properties of these quasi-monodimensional materials.

A photoelectron spectroscopic study has also been carried out[78] on 4:4′-bi(2,6-diphenyl-1-thiopyranylidene) **2f**, and the polyiodides salts **2f**-$I_{2.28}$, **2f**-$I_{3.33}$, **2f**-I_6 as well as on the corresponding diperchlorate. It shows that the electrical conductivity of these materials is related to charge delocalisation over the whole thiopyranylidene ring.

5. CHARGE TRANSFER COMPLEXES AND RADICAL ION SALTS FROM 2:2′-BI(4,6-DIARYL-1-THIOPYRANYLIDENES)

2:2′-Bi(4,6-diaryl-l-thiopyranylidenes) **3** (Ar = C_6H_5, **3f**; Ar = p-$CH_3C_6H_4$, **3g**; Ar = p-ClC_6H_4, **3k**) give charge transfer complexes with TCNQ. Some of them possess relatively high conductivities at room temperature.[33,36] In the same way the complex **3k**-TCNQ[33] has a conductivity of 0.2 S cm^{-1} as compacted powder and its optical spectrum displays, among others, an absorption band towards 3600 cm^{-1} (0.44 eV), characteristic of organic conductors.[64] 2:2′-Bi-(4,6-diphenyl-1-thiopyranylidene) **3f** gives with iodine a radical ion salt of the stoichiometry **3f**-$I_{2.4}$ of which the electrical properties of a single crystal have been determined [$\sigma_{r.t.}$ = 10 S cm^{-1}]; it is a semiconductor with an activation energy of 0.046 eV between room temperature and 170 K and of 0.018 eV below 170 K.[36,86] The XPS spectra of the donor **3f** and its derivatives with TCNQ, iodine and bromine have been determined and analysed.[87]

6. CHARGE TRANSFER COMPLEXES OF 4:4′-BI(SELENOPYRANYLIDENES) WITH TCNQ

4:4′-Bi(selenopyranylidenes) **4** give charge transfer complexes with TCNQ by direct oxidation in methylene chloride. The characteristics are listed in Table

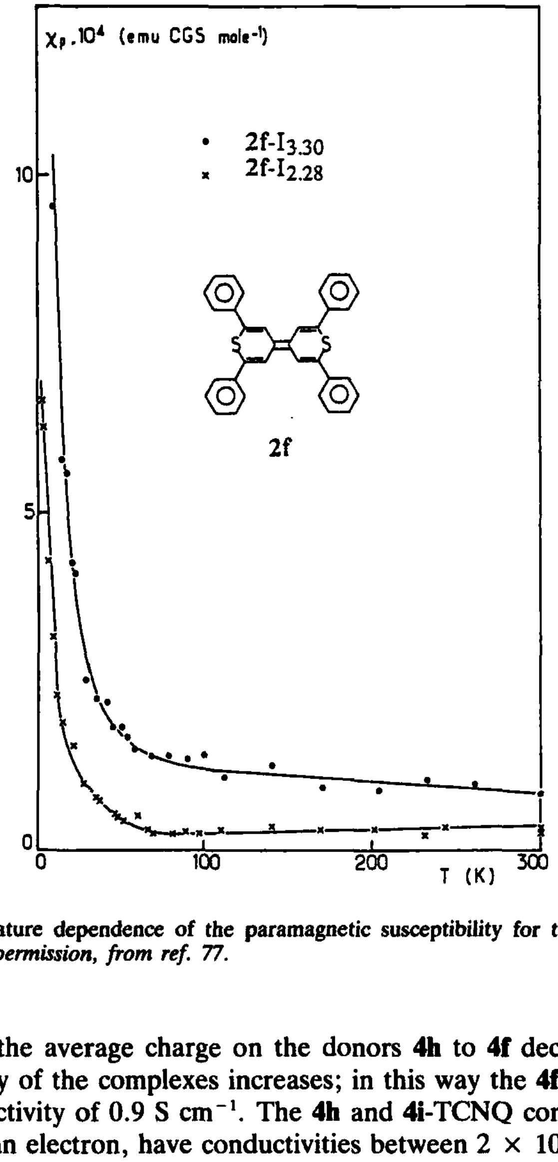


FIGURE 5 Temperature dependence of the paramagnetic susceptibility for the **2f**-I$_{3.30}$ and **2f**-I$_{2.28}$ salts. *Reprinted, by permission, from ref. 77.*

9.[33,37–39,88] When the average charge on the donors **4h** to **4f** decreases, the electrical conductivity of the complexes increases; in this way the **4f**-TCNQ complex displays a conductivity of 0.9 S cm^{-1}. The **4h** and **4i**-TCNQ complexes in which the donor loses an electron, have conductivities between 2 × 10^{-3} and 5 × 10^{-3} S cm^{-1}. [The complex (**4b**)$_2$-TCNQ$_3$ on account of its stoichiometry implies a nearly total electronic transfer (0.9) from the donor[39]].

The optical absorption spectra in the solid state display in addition to the bands due to the donors and TCNQ, interband transitions towards 12 000–13 000 cm^{-1} (1.48–1.60 eV). In the 2 000–3 500 cm^{-1} (0.25–0.43 eV) range there is a band assigned as A[64] or CT$_2$[89] due to an intraband transition in the TCNQ stacks characteristic of organic conductors.[5]

The specular reflectance spectrum of the **4f**-TCNQ complex, determined on compacted powder, displays a maximum reflectivity of about 30% in the 4 000–

TABLE 9 Charge transfer complexes of 4:4′-bi(selenopyranylidenes) with TCNQ.

Donor	Stoichiometry $(4)_x$-$(TCNQ)_y$	Charge transfer ρ	Optical Spectra ν (cm^{-1})	Conductivity $\sigma_{r.t.}$ ($S\ cm^{-1}$)
4b	$x = 2; y = 3$	0.6	2 500	1.4×10^{-2}
4f	$x = y = 1$	0.7	2 050	0.9
4g	$x = y = 1$	0.8	1 950	0.3
4h	$x = y = 1$	1	3 450	2×10^{-2}
4i	$x = 1; y = 0.8$	1	—	5×10^{-3}

-The stoichiometries were determined by elemental analysis.
-The charge transfer degree ρ was calculated from the ν_{CN} value[90]
-The conductivities were measured on compacted powder.

10 000 nm (0.31–0.12 eV) range up to the Drude edge around 2 000 nm, similar to TTF-TCNQ. The parametrization of the reflectance graph according to Drude's model for metals coupled with one Lorentz oscillator in the 1 010–3 810 nm range reproduces the experimental data in the 1 010–6 000 nm range (Fig. 6) and leads to an optical conductivity at zero frequency of 480 S cm^{-1}.[39]

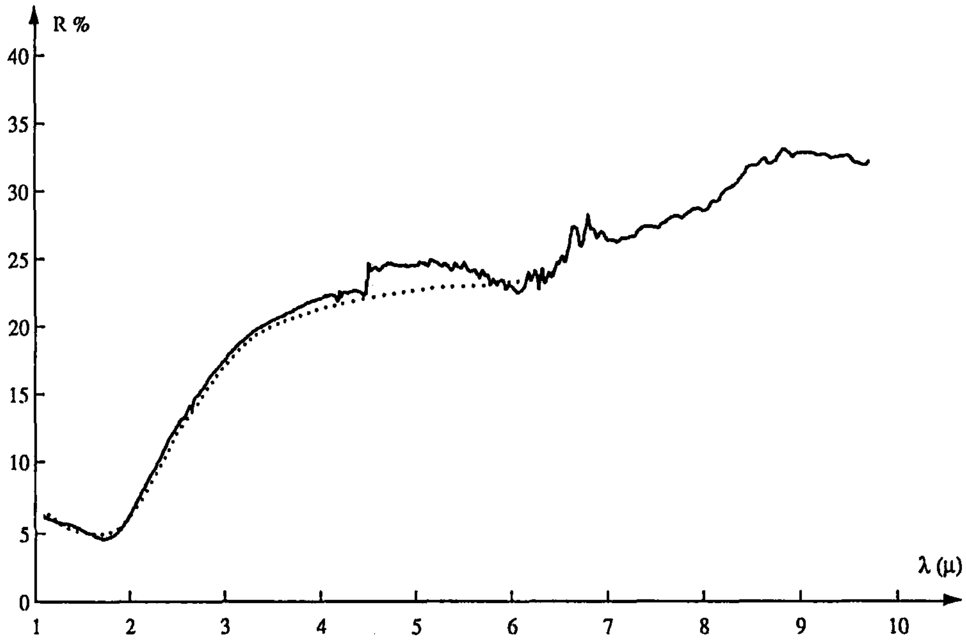


FIGURE 6 Optical reflectivity curves of **4f**-TCNQ
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—— Experimental
····· *Parametrization*

The static paramagnetic susceptibility value of this complex is 2.1×10^{-4} uem/mol at room temperature, its variation as a function of temperature seems to confirm that this complex would be metallic up to 120 K where a metal-insulator transition would take place. The rise in paramagnetic susceptibility at low temperature (T < 68 K) could be attributed to chemisorbed oxygen,[39] (Fig. 7).

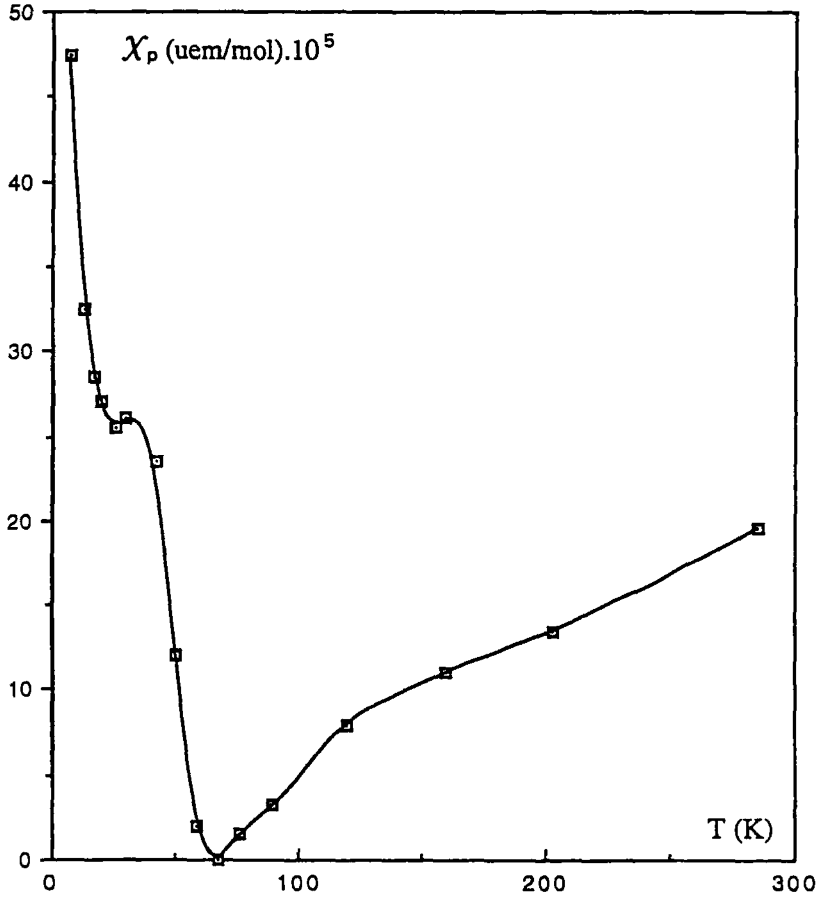

FIGURE 7 Static paramagnetic susceptibility variation; of **4f**-TCNQ
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7. RADICAL ION SALTS OF 4:4'-BI(SELENOPYRANYLIDENES) WITH IODINE

7.1. *Synthesis and Structure*

The radical ion salts of 4:4'-bi(selenopyranylidenes) **4** are prepared by direct oxidation with iodine in methylene chloride. For every type of donor **4**, several polyiodides are obtained. The stoichiometry depends on the molecular ratios of the reagents[91] (Table 10). A crystallographic X-ray diffraction study has been carried out on the **4f**-I_2 salt, (Fig. 8). The results show that in the quadratic crystalline form, the donor molecules stack in a regular and parallel mode along the c axis. The I_3^- anions form chains in the channels which exist between the donor columns.[91,95]

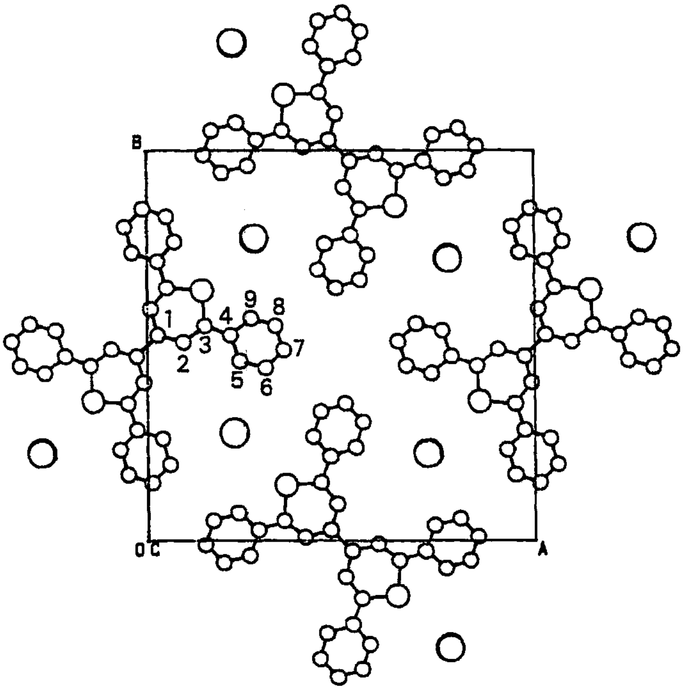

FIGURE 8 Projection of **4f**-I_2 along the c axis.[95]
○ I ○ Se

TABLE 10 Radical ion salts of 4:4'-bi(selenopyranylidenes) with iodine: **4**-I_x[91]

Donor	Molar ratio $m = [I_2]/4$	Stoichiometry	Conductivity $\sigma_{r.t.}$ S cm^{-1}
4b	m = 0.5	x = 1.8	1.9×10^{-6}
4b	m = 2.5	x = 5.6	1.8×10^{-7}
4f	m = 0.5	x = 2	0.13
4f	m = 1	x = 3.5	0.04
4f	m = 2.5	x = 5.9	5×10^{-4}
4g	m = 0.5	x = 1.9	0.02
4g	m = 2.5	x = 5.9	1.5×10^{-5}
4h	m = 0.5	x = 2.9	0.03
4h	m = 2.5	x = 5.4	3.2×10^{-3}

The conductivities were measured on compacted powders.

7.2. *Optical Properties*

A Raman spectroscopic study of the **4f**-$I_{3.5}$ and **4f**-$I_{5.9}$ salts shows the presence of I_3^- (peak at 107 cm^{-1}) and I_5^- (peak at 155 cm^{-1}) species.[91] The absorption spectra in the solid state of the iodide salts **4**-I_x have been determined in the 40 000 cm^{-1} (4.94 eV) to 200 cm^{-1} (0.025 eV) range.[91] They generally display one or two charge transfer bands in the 2 000 cm^{-1} (0.25 eV)–13 000 cm^{-1} (1.6 eV) region; the one situated below 10 000 cm^{-1} is shifted toward lower energies when the donor-iodine ratio decreases, thus the **4f**-I_2 salt shows an intervalent charge transfer band at 2 000 cm^{-1}, characteristic of a metallic salt, while the semiconductor salt band lies around 4 000 cm^{-1} [**4f**-$I_{3.5}$ and **4f**-$I_{5.9}$].[50,91]

The specular reflectivity of the **4f**-I_x salts, (Fig. 9), shows that the **4f**-$I_{3.5}$ and **4f**-$I_{5.9}$ salts have a reflectivity maximum of 15% and 12%, respectively. They decrease in the infrared range. This behaviour characterizes a semiconductor state. On the other hand, the **4f**-I_2 spectrum (Fig. 10) displays a maximum reflectivity of about 25% in the infrared region [2 500 to 1 000 cm^{-1}] up to the Drude edge at 3 000 nm [3 333 cm^{-1}–0.41 eV], characteristic of an organic metal, similar to the one of the TTF-TCNQ complex determined under the same conditions.[92] The parametrization of this iodide salt spectrum with Drude's model to which Lorentz oscillators are associated allows to obtain the optical conductivity at zero frequency: σ_{opt} = 541 S cm^{-1}.[91] The optical conductivity of this salt is higher than that of its sulfur analogue [**2f**-$I_{2.28}$: σ_{opt} = 320 S cm^{-1}, $\sigma_{r.t.}$ = 250 S cm^{-1}].[66]

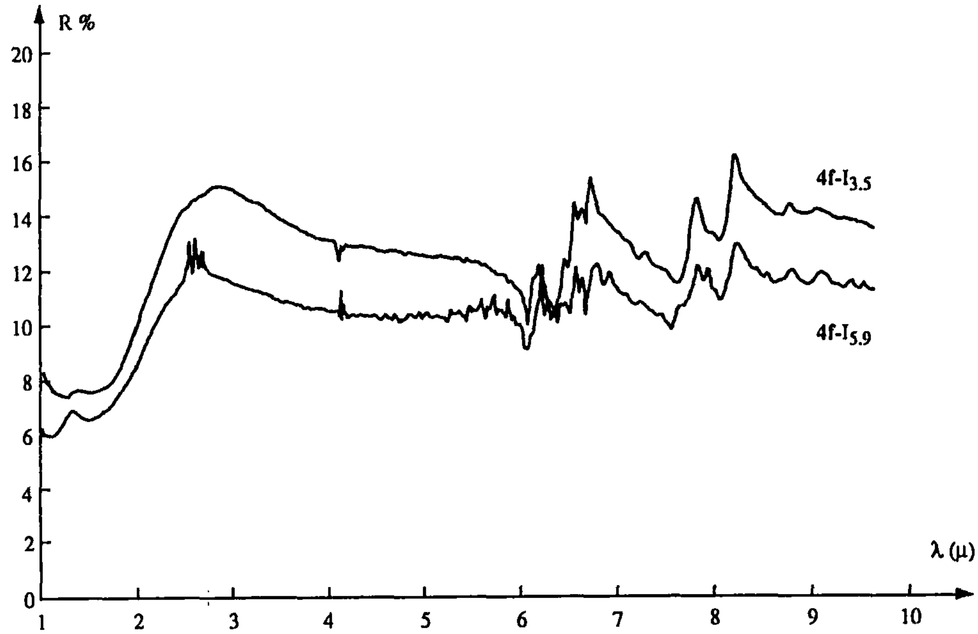

FIGURE 9 Optical reflectivity curves of **4f**-$I_{3.5}$ and **4f**-$I_{5.9}$ *Reprinted, by permission, from ref. 91.*

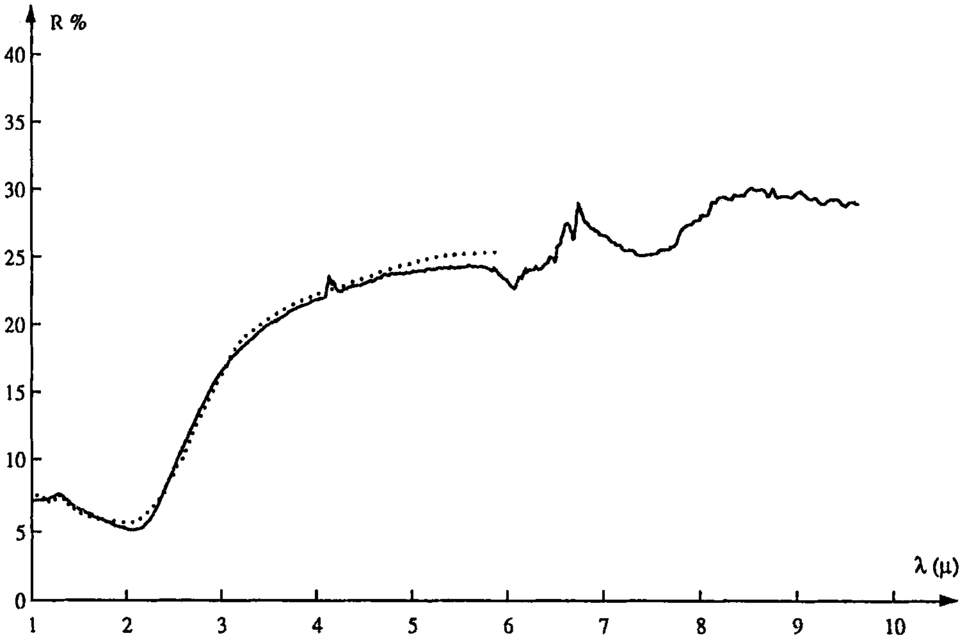

FIGURE 10 Optical reflectivity curves of **4f**-I_2
Reprinted, by permission, from ref. 91

——— Experimental
····· Parametrization

7.3. *Electrical and Magnetic Properties*

The electrical conductivity of a single crystal, $\sigma_{r.t.} = 4\ S\ cm^{-1}$ of the **4f**-$I_{3.5}$ salt has been determined as a function of temperature from 115 K to 225 K.[91] We observe a semiconductor behaviour with a forbidden band width of 0.2 eV (Fig. 11). The most conducting salt, **4f**-I_2, displays a very weak variation in paramagnetic susceptibility with temperature in the 300–90 K range, while the semiconductor salt **4f**-$I_{3.5}$ has a paramagnetic susceptibility which decreases more quickly in this same range; this confirms the organic metal character of the **4f**-I_2 salt since conductors possess paramagnetism nearly independent of temperature. One notes, as already observed for the TCNQ-4:4′-bi(chalcogenopyranylidenes) complexes, that the paramagnetic susceptibility of the **4f**-I_2, **4f**-$I_{3.5}$ and **4f**-$I_{5.9}$ salts increases at lower temperatures,[91] probably due to the presence of chemisorbed oxygen.[39,63,77]

8. LIQUID CRYSTALS FROM 4:4′-BI(PYRANYLIDENES), 4:4′-BI(THIOPYRANYLIDENES), 4:4′-BI(SELENOPYRANYLIDENES) AND THEIR CHARGE TRANSFER COMPLEXES

4:4′-Bi(pyranylidenes) and 4:4′-bi(thiopyranylidenes) substituted by phenyl groups with long chains in the para position generally display a columnar struc-

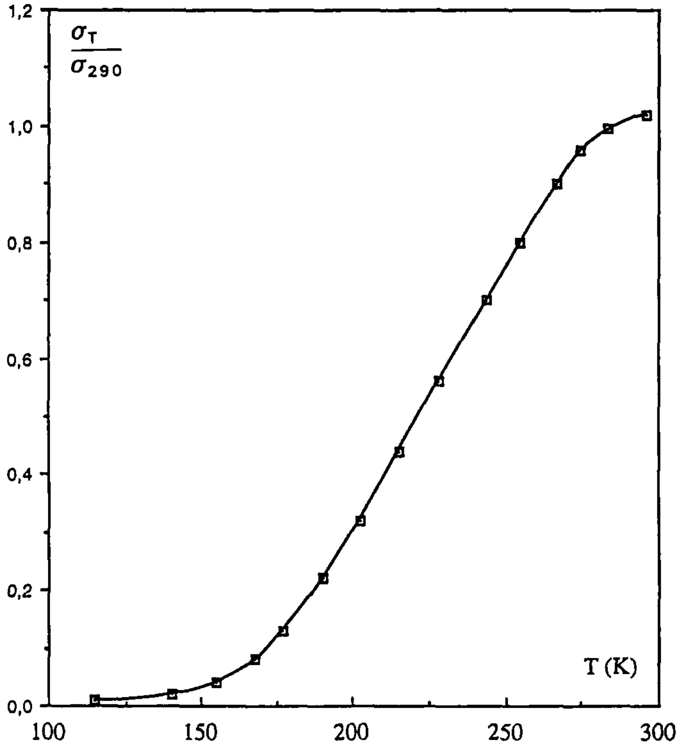

FIGURE 11 Conductivity variation of **4f**-$I_{3.5}$ (single crystal)
Reprinted, by permission, from ref. 91.

ture.[30,31,79–83] 4:4′-Bi(2,6-diarylpyranylidenes) and 4:4′-bi(2,6-diaryl-1-thiopyranylidenes) with *n*-alkyl substituents: C_nH_{2n+1} display mesophases when $n > 9$; in the case of an alkoxy substituent, only 4:4′-bi(2,6-di-*p*-dodecyloxyphenyl-1-thiopyranylidene) displays a mesophase.[31,83] Upon association of these donors with TCNQ, some of the complexes obtained possess a liquid crystal structure, for example the complex of stoichiometry 1:1 between 4:4′-bi(2,6-di-*p*-dodecyloxyphenyl-1-thiopyranylidene) and TCNQ is a mesomorphic conductor [$\sigma_{r.t.} \approx 0.7$ S cm^{-1} on single crystal][81,82,84] which displays a lamellar smectic mesophase between 120 °C and 154 °C[82] and which remains conducting in the mesophase ($\sigma \approx 10^{-3}$ S cm^{-1}), even above the transition temperature (120 °C).[85]

4:4′-Bi-(2,6-diaryl-1-selenopyranylidenes) with aryl groups substituted in the para position with long alkyl, **4n** and **4p**, alkoxy, **43** and alkylthio groups, **44**, have been prepared in order to study the influence of the nature and the presence of the heteroatom and of the length of the chain on the mesomorphic behaviour. Compound **43** ($n = 12$) possesses a lamellar structure and gives a charge transfer complex with DDQ ($\sigma = 4 \times 10^{-5}$ S cm^{-1}) which displays crystalline transition phases without mesomorphic properties.[94]

9. CHARGE TRANSFER COMPLEXES OF 4:4'-BI(TELLUROPYRANYLIDENES)

4:4'-Bi(telluropyranylidenes) **5** give several stoichiometric complexes with TCNQ, depending on the relative proportion of the donor and TCNQ as well as the experimental conditions used (solvent, temperature). The complexes obtained are listed in Table 11.

TABLE 11 Charge transfer complexes from 4:4'-bi(telluropyranylidenes) and TCNQ: $(\mathbf{5})_x$-$(TCNQ)_y$

Donor	Stoichiometry $\mathbf{5}_x$-$(TCNQ)_y$	Conductivity $\sigma_{r.t.}$ (S cm^{-1})	References
5b	x = 1; y = 2	4	93
5b	x = 2; y = 3	0.4	93
5f	x = y = 1	0.5	93
5g	x = 1; y = 0.9	1	39

The conductivities were measured on compacted powders.

The 4:4'-bi(2,6-di-*p*-tolyl-l-telluropyranylidene)-TCNQ complex **5g**-$(TCNQ)_{0.9}$ has a degree of charge transfer of 0.7 and its absorption spectrum displays a band called "A" at 2 040 cm^{-1}.[39] The optical reflectivity graph shows an increase in its reflectivity from a minimum at 2 074 nm (4 822 cm^{-1}, 0.60 eV) to 9 000 nm (1 111 cm^{-1}, 0.14 eV). The analysis of this spectrum by Drude's model with two Lorentz oscillators associated gives an optical conductivity at zero frequency: σ_{opt} = 193 S cm^{-1},[39] characteristic of a conductor. Some radical ion salts are obtained from the donors **5b**, **5d** and **5f** (perchlorate and tetrafluoroborate) with 2:3 stoichiometry; the conductivity values of the compacted powders are about 10^{-4} S cm^{-1}.[93]

CONCLUDING REMARKS

The present survey shows the interesting properties of the bi(chalcogenopyranylidenes) series. These quasi-planar heterocycles with low oxidation potential values are good electron π donors and lead to organic conducting materials. Some of them, especially the sulfur and selenium derivatives with larger orbitals, give charge transfer complexes and radical ion salts with metallic behaviour. The tellurium derivatives do not exhibit an increase of the metallic properties, probably due to a larger deformation of the heterocyclic system.

In the field of "organic metals", further work on the synthesis and properties of 4:4'-bi(chalcogenopyranylidenes) and their radical ion salts remains an interesting research area in the years to come.

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